

✓COMPLEXING BEHAVIOURS
of
2-THIOPYRROLE-1,2-DICARBOXIMIDE AND
N-CARBAMOYLPYRROLE-2-THIOCARBOXAMIDE

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
RAY SAHEB

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
FEBRUARY, 1983

1952

DEDICATED

TO
↓ ↓ ↓
* * *

PROFESSOR U.C. AGARWALA, F.N.A.

*whom I owe more to aim than to
express, even indicate, in words.....*

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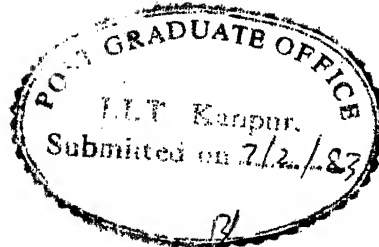
STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Dr. S.K. Dikshit.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.


Ray Saheb

Kanpur;
February 1983.



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CERTIFICATE I

Certified that the work contained in this thesis,
entitled: COMPLEXING BEHAVIOURS OF 2-THIOPYRROLE-1,2-
DICARBOXIMIDE AND N-CARBAMOYLPYRROLE-2-THIOCARBOXAMIDE,
has been carried out by Mr. Ray Saheb under my supervision
and the same has not been submitted elsewhere for a degree

S.K. Dikshit

(S.K. Dikshit)

Thesis Supervisor

Kanpur;

February 1983.

5-12-1983

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DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that Mr. Ray Saheb has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 511 Physical Organic Chemistry
Chm 521 Chemical binding
Chm 524 Modern Physical Methods in Chemistry
Chm 541 Advanced Inorganic Chemistry I
Chm 800 General Seminar
Chm 801 Graduate Seminar
Chm 900 Post-Graduate Research

Mr. Ray Saheb was admitted to the candidacy of the Ph.D. degree programme in January 1979 after he successfully completed the written and oral qualifying examinations.

U. Agarwala
(U.C. Agarwala)
Professor and Head,
Department of Chemistry,
IIT-Kanpur

S. Chandrasakaran
(S. Chandrasakaran)
Convener,
Departmental Post-Graduate-
Committee
IIT - Kanpur

ACKNOWLEDGEMENTS

It gives me an immense pleasure to express my gratefulness towards Dr. S.K. Dikshit, Assistant Professor in the Dept. of Chemistry, I.I.T., Kanpur for giving me a chance to work on this problem. His invaluable suggestions, constructive comments and useful discussions throughout the present investigations led to the completion of this work. His keen interest in my personal welfare is thankfully acknowledged.

I am indebted to my lab colleagues Dr. Okhil Medhi, Dr. T. Singh, Dr. R. Parashad, Dr. K.K. Pandey, Dr. S. Datta, Dr. K.C. Jain and messrs R.D. Tewari, S.K.S. Yadav, P.K. Srivastava, K.S. Arulsamy, D.K.M. Raju, M.I. Khan, K.N. Udupa, R.F.N. Ashok, S. Sriram, B.R. Srinivasan and H.K. Gupta for their pleasant association and ready help and cooperation all the time.

My sincere thanks are due to Dr. I.P. Khullar for his fruitful suggestions and timely advise.

I am thankful to all the staff members for their cooperation specially to messrs K. Rajgopalan, S.K. Sinha, A.H. Siddiqui, N. Ahmad and R.K. Jain (Physics Dept.) for recording IR, Electronic spectra and C, H, N analyses.

Help received through discussions with Mr. O.P. Lamba and S. Ram of Physics Dept., IIT-Kanpur is highly appreciated.

PREFACE

During the past three decades one of the major problems facing the inorganic chemists is to understand the nature of interaction of metal ions in various oxidation states with soft donors like sulphur under various bonded conditions. Even today this is an outrageously difficult situation even if it were not awesome for the growth of the field. Added to this, the recent observations of involvement of sulphur containing molecules in conjunction with a few transition metal ions in various enzymatic and metabolic processes have given a further challenge to the chemists. Designing of the sulphur containing model molecules mimicing those involved in natural processes ranks among the prime goals of inorganic chemistry. Today what is lacking is the integrated view of the large volume of disorganized experimental data. Any attempt in this direction leads to a number of gaps in the rationalization process. The attempts to resolve this dilemma is to recognize that possibly more observations are needed before the achievement of the long awaited goal. The present thesis is only a little attempt in this direction. The work concerns mainly the study of the complexing behaviours of 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH) with various soft and border line-soft metal ions in various oxidation states and the assignments of the geometries to the corresponding molecules.

The first chapter, after defining the objectives and scope of the work, provides an upto date interaction when viewed as acceptor-donor behaviour. Having discussed this, a brief account of the complexing behaviour of the ligands analogous to ones described herein has also been discussed for a comparative study.

The interactions of the soft metal ions, Cu(I), Ag(I), Hg(II), Cd(II) and Pb(II) lead to desulphurization of the ligand affording the metal sulphides and literature known oxygenated ligands. It is interesting to note that these metal ions prefer to form metal sulphide rather than complexing with oxygenated ^{ion}~~ated~~ ligands. The rate of reactions vary depending upon the nature of the metal ion, because of which the separation of silver(I) complex of the sulphur ligand became possible. The discussion of the reactions and their other aspects have also been given (Chapter II).

Third chapter focuses the formation of the relatively less known diamagnetic complexes of cobalt(II) with the chosen ligands in the presence and in the absence of nitrogen containing bases. The diamagnetic behaviours of $[\text{CoL}_2\text{B}]$ and $[\text{CoL}_2]$, where L and B represent the ligand and the base, respectively are explained in terms of the square pyramidal or square planar geometries respectively with ligands having large crystal field and the antiferromagnetic interaction of Co(II) ions. However, trigonal bipyramidal geometries are also a possibility.

The interactions of Ni(II) and Cu(II) ions with the ligands have been discussed in Chapter IV. Nickel forms square pyramidal (or trigonal bipyramidal) complexes with TPH while with CPTH it forms square planar complex. Copper(II) is reduced to copper(I) which gave diamagnetic complexes which were assigned a linear geometry.

Fifth chapter presents the reactions of TPH and CPTH with Pd(0), Pd(II), Pt(IV), Rh(I), Rh(III) and Ru(III) ions. Rh(III) and Ru(III) are ~~getting~~ reduced to Ru(II) and Rh(I) in their complexes which were assigned ~~a~~ octahedral and square planar geometries, respectively. Palladium and platinum gave $(PdL_2)_n$ type complexes, where L represents the ligand. All the complexes described in this thesis have been characterised on the basis of analytical data, spectral (IR, UV and Visible) and magnetic measurement studies.

Chapter six briefly summarizes the overall work presented in the thesis.

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CHAPTER I

INTRODUCTION

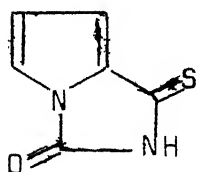
OBJECT AND SCOPE OF THE WORK

The ligation behaviour of elementary sulphur and its derivatives is concerned with the chemistry of a large number of complexes whose stability ranges from that of minerals to species with life times of less than a millisecond. Although the synthetic procedures and the qualitative properties of metal ion complexes with sulphur containing ligands have long been known, but one of the major unsolved problems of inorganic chemistry has been that of rationalization of the various experimental facts utilizing the principles of the existing bonding theories. During the two decades that have just

elapsed, the application to understand the nature of metal to sulphur linkage has resulted in no more than a little systematization of the various data relating to metal sulphur bond. Since the contradictory rationalizations are more often encountered in the field, it can not, however, be claimed that the solution is complete. Thus, efforts are still needed for the development of a unified picture of the nature of M-S bond under different conditions so that a foundation could be laid to correlate a vast catalogue of apparently unrelated observations. In addition, an interesting facet revealed during such a study is the revelation that the metal sulphur interaction plays a very important role not only in the biological processes, but also they possess important pharmacological properties as well. Thus, a few metal ion complexes have been found to have anticarcinogenous¹⁻⁸ and antiviral⁹⁻¹⁶ properties. This fascinating subject looms so large on the horizon of coordination chemistry that a new direction has been given to the field of metal-sulphur ligand complex chemistry. One such area under development in this field is to design and synthesize the ligands which could bind metal ions to yield complexes where one encounters their behaviours similar to the ones found in biological systems. Obviously, this behaviour should be characteristic of the coordination of the metal ion, the stereochemistry, the conformation of the complex and the nature of the bond formed between the metal ion and donor centre of the ligand. An understanding is,

therefore, needed to know the relationship between the various properties of the complexes so that their structures and the reactions could be interpreted. The present work is only an attempt in this direction. This might broaden a little the understanding of: (i) the donor properties of sulphur containing ligands in general, (ii) the nature of metal-sulphur linkage, (iii) the positions of the metals and the ligands in the nephelauxetic and spectrochemical series, (iv) the stereochemistry and coordination number of the transition metal ions, and (v) the stability of square planar complexes with the ligands having delocalised π -electron system.

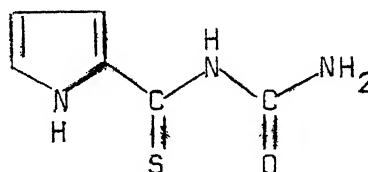
With the above objectives in mind the following ligands have been selected for the present study:



2-Thiopyrrole-1,2-dicarboximide

I

and



N-Carbamoylpyrrole-2-thio-carboxamide

II

An important aspect of these ligands is their being polyfunctional in nature, having nitrogen, oxygen and sulphur as potential donors. Given the various alternative modes of linkages these ligands could utilize for the complex formation, they can behave as monodentate or bidentate ligand utilizing

one or two of their donor sites respectively. The possibility of simultaneous involvement of more than two donor atoms for coordination is by far the most unlikely because of the very high energy required for the orientation of all the donor atoms such as to form a favourable surrounding for binding to the same metal ion. Which of the donor sites will be preferred by the metal ion for binding depends, quite obviously, more on the nature of metal ion, its oxidation state and to a lesser degree on the ligand and its substituents. A similar dependency on the metal/ligand combination is expected for the stability of the complex or chelate formed. It will, therefore, be worthwhile to study the complexing behaviour of such a system with various metal ions in different oxidation states. The metal ions taken up for such a study include Co(II), Co(III), Ni(II), Cu(I), Cu(II), Ag(I), Cd(II), Hg(II), Pb(II), Rh(I), Rh(III), Ru(III), Pd(0), Pd(II) and Pt(IV). The modes and the nature of the bond formed by the various metal ions have been studied by the infra-red, electronic spectral and the magnetic susceptibility studies. Their possible structures have been tentatively proposed. The data have been briefly summarized in Table I.1.

Although a possibility of an extremely ionic or covalent bond formation by the interaction of an acid and base does not exist, but when the base is a sulphur ligand, such a possibility is far remote because of the varying differences in the electronegativities of sulphur ligands and the metal ions. It is,

Table I.1

Formula, Structure, Bonding and Colour of the Complexes
(In every case metal is bonded through
-C(S)NHC(O)- moiety of the ligand)

Complex	Structure	Bonding	Colour
1	2	3	4
Cu(TPH)Cl	Linear	A	Dark brown
[Cu(PPh ₃) ₂ (TPH)Cl]	Tetrahedral	A	Dark red
Cu(CPT)	Linear, poly	A	Greenish yellow
Ag(TP)	- do -	B	Yellow
Ag(CPT)	- do -	B	Yellow
(TPH) ¹	-	-	Yellow
(CPTH) ¹	-	-	Yellow
[Co(TP) ₂ Py] ₂ ·4H ₂ O	Square pyramidal	C	Black brown
[Co(TP) ₂ ·Imid] ₂	- do -	C	Red brown
[Co(TP) ₂ β(γ)pic] ₂	- do -	C	Red brown
[Co(TP) ₂] ₂ ·2H ₂ O	Square planar	C	Black brown
[Co(CPT) ₂] ₂	- do -	C	Red
[Co(CPT) ₂ Py] ₂	Square pyramidal	C	Yellow
[Co(CPT) ₂ ·Imid] ₂	- do -	C	Yellow
[Co(CPT) ₂ β(γ)pic] ₂	- do -	C	Yellow
[Co(Py)₄Cl₂]	Octahedral	-	Green
[Ni(TP) ₂ Py]·2H ₂ O	Square pyramidal or trigonal bipyramidal	D	Red
[Ni(TP) ₂ β(γ)pic]·H ₂ O	- do -	D	Red brown
[Ni(TP) ₂ ·Imid]·2H ₂ O	- do -	D	Red brown

...contd.

Table I.1 (contd.)

1	2	3	4
$\text{Cu}(\text{TP})(\text{TPH})\text{Py} \cdot \text{H}_2\text{O}$	Linear or Tetrahedral, poly	B	Red
$\text{Cu}(\text{TP})(\text{TPH}) \cdot \text{Imid} \cdot \text{H}_2\text{O}$	- do -	B	Red brown
$\text{Ni}(\text{CPT})_2$	Square planar	C	Red
$\text{Cu}(\text{CPT})(\text{CPTH}) \cdot \text{H}_2\text{O}$	Linear, poly	A	Yellow
$\text{Ru}(\text{TP})_2$	Octahedral, poly	E	Black brown
$\text{Rh}(\text{TP})(\text{TPH})$	Square planar	F	Brown
$[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2$	- do -	G	Brown
$\text{Pd}(\text{TP})_2$	- do -	H	Red brown
$\text{Pt}(\text{TP})_2 \cdot \text{H}_2\text{O}$	- do -	H	Red brown
$\text{Ru}(\text{CPTH})_2\text{Cl}_2$	Octahedral, poly	I	Black
$\text{Rh}(\text{CPT})(\text{CPTH})$	Square planar	J	Yellow
$\text{Pd}(\text{CPT})_2$	- do -	H	Yellow
$\text{Pt}(\text{CPT})_2$	- do -	H	Yellow

$(\text{TPH})^1$ = 2-pyrrole-1,2-dicarboximide; $(\text{CPTH})^1$ = N-carbamoyl-pyrrole-2-carboxamide; Py = pyridine; pic = picoline; Imid = imidazole; poly = polymeric.

A = Ligand is acting as unidentate and bonded through N.

B = Ligand is acting as bidentate and bonded through N and S.

C = Ligand is acting as bidentate chelate and bonded through N and O with Co---Co interaction.

D = Ligand is acting as bidentate chelate and bonded through N and O and the base bonded through nitrogen.

...contd.

Table I.1 (contd.)

-
- E = Two ligand molecules are acting as bidentate chelate and bonded through N and O while the two acting as unidentate and bonded through S atom to the same metal atom.
- F = Two ligand molecules are acting as bidentate chelate bonded through N and O and the S atom is bonded through next atom of the metal.
- G = Ligand is acting as unidentate and bonded through carbonyl oxygen with chloride bridges between two metal atoms.
- H = Ligand molecules are acting as unidentate. Two ligand molecules are bonded through N while the other two through O.
- I = Ligand is acting as bidentate chelate and bonded through S and O atoms with chloride bridges between two metal atoms.
- J = One ligand molecule is acting as bidentate chelate bonded through S and O and the second and third molecules as unidentate bonded through N and O atoms, respectively.
-

however, obvious that the metal-sulphur bond should have partial ionic and partial covalent character and the degree of ionicity or covalency in it is function of the metal ion and substituents attached to the sulphur donor atom. What factors govern the partial covalency in it and how much do they contribute in a particular complex are still a matter of controversy. It will, therefore, not be out of place to briefly review the present positions of the understanding of the nature of such a bond. The following paragraphs give a very concise account of it.

General Characteristics of M-S Bond

An interaction between two atoms is a function of the nature of the interacting species, thereby the stability of the bond should depend upon factors like their electronegativity, the degree of overlap of the orbitals, sizes of the atoms or ions, the number and the nature of the substituents linked to the interacting atoms. Since both particles contribute significantly to the nature of the bond, the metal-sulphur bond will be viewed under two separate heads: (a) the role of sulphur as donor atom in relation to other donors and (b) the relative affinities of various metal ions for elementary sulphide ion and for sulphur containing ligands.

(a) Sulphur as donor atom:

There are great differences between the ligation properties of sulphur and those of the first row elements. Differences from

these elements are attributable to the following factors besides some others:

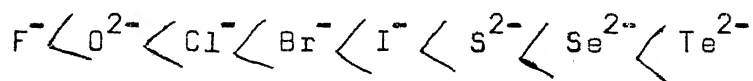
(i) The lower electronegativity which lessens the relative ionic character of the M-sulphur bond, alters the relative stabilities of various kinds of bonds.

(ii) The availability of low lying empty d-orbitals which may be able to participate in the π -backbonding by their overlap with the filled d-orbitals of the metal ions. This type of π -backbonding is not possible between metal ions with no or a few electrons in the d orbitals and ligands having π orbitals ^{not forming π -system} as donor atoms because of the absence of low lying vacant orbitals for accepting metal d-electrons. Ahrlund¹⁷ has pointed out the presence of filled or nearly filled d-orbitals on the metal ions as one of the condition for π -backbonding. Although there is another possibility of π -bond formation by the overlap of the filled ligand π -orbitals with metal empty d-orbitals, this type of interaction is, however, ^{not} important in most complexes because of the accumulation of excess negative charge on the metal ion through σ and π -systems. It could be important only in complexes of metal ions having extremely high charge like CrO_4^{2-} , TaF_8^- etc.

Howsoever logical this explanation of π -backbonding may be for the preferential bonding of sulphur with a certain metal ions, it did not appeal to Jørgensen because of the absence of the spectroscopic data suggesting low lying orbitals in these

sulphur complexes. In addition, recently molecular orbital calculations on organic molecules having thioether sulphur atom failed to detect the importance of d-orbital participation in reactions unique to sulphur.^{18,19} The same calculations favoured the polarizability of the nonbonded electrons in the 3p orbitals of sulphur to explain the reactions of carbon atoms in the vicinity of thioether sulphur atom. In the number of other cases where this question is examined, it seems apparent that both d-orbital participation and the polarizability of sulphur nonbonded electrons are important. It is, therefore, difficult to predict the dominance of one or the other influence and thus problem is still unsettled.

(iii) Relatively high polarizability of sulphur which enhances the relative covalent character in the M-S bond. The polarizability of sulphur falls as follows:



which is just the electronegativity series in the reverse order. Since sulphur atom has got more polarizability than O, Cl, Br and F, M-S bond will, therefore, have more covalent character than M-O, M-Cl or M-Br bond. This statement is true only in those cases where the donor atoms are acting as ligand in the form of elementary ions. Generally, donor atoms eg., N and S exist in the combined state, thereby their polarizability should be different because of the presence of other atoms or groups

attached to the donor atoms (N and S) resulting in the change of covalent character of the bond as compared to that when they are bonded as elementary ions. Fajan^{20,21} stated in his theory of quanticules that the relative polarity of two adjacent bonded atoms depends not only on the polarization properties of two atoms, but also on their quantization.

A comparison of the permanent dipole moments and the coordinating ability of neutral oxygen ligands shows a decrease in the order $\text{H}_2\text{O} > \text{ROH} > \text{R}_2\text{O}$ while the dipole moment and coordinating ability for sulphur ligands increase in the order²²⁻²⁵ $\text{H}_2\text{S} < \text{RSH} < \text{R}_2\text{S}$. In addition, if the effects of π -backbonding are ignored, the coordinating ability of a series of R_2X ligands decrease in the order $\text{R}_2\text{O} > \text{R}_2\text{S} > \text{R}_2\text{Se} > \text{R}_2\text{Te}$. The coordinating ability of S^{2-} , RS^- and R_2S depends on the polarizability and the number of lone pair of electrons on the sulphur atom. Both these factors decrease in the order $\text{S}^{2-} > \text{RS}^- > \text{R}_2\text{S}$ and therefore, the wide distinction among the above three ligands is based not only on the polarizability, but also on the number of lone pairs available on the sulphur atom.²⁶ Williams²⁷ considers that the principal difference between thiols and thioether as ligands is that the sulphur in the former is relatively more polarizable but not as effective d_π -electron acceptor as that in the latter. Jørgensen²⁸ has placed R_2S in the spectrochemical series between H_2O and NH_3 : $\text{H}_2\text{O} > \text{NH}_3 > \text{R}_2\text{S} > \text{H}_2\text{O}$ and RS^- between F^- and Cl^- : $\text{F}^- > \text{RS}^- > \text{Cl}^-$. The position of the

ligand, HS^- , is expected to be similar to that of RS^- in the spectrochemical series.

The known low affinity of neutral sulphur ligands for H^+ [i.e., pK for $(\text{CH}_3)_2\text{S} = -5.2$]²⁹ suggests that they will be weak ligands for class (a) metal ions and stable metal complexes with neutral sulphur ligands if they exist, should be found among class (B) metal ions.³⁰ Within class (b) the members of the sub-group that includes low oxidation states, especially metal ions with filled or near filled $d\pi$ electrons are expected to form stable complexes with neutral sulphur ligands because of the additional stability due to $\text{M} \rightarrow \text{L}$ π -backbonding. As mentioned in the preceding paragraphs, among R_2S , RSH and H_2S ligands, the most stable complexes are formed by R_2S . The neutral ligands RSH and H_2S form weaker complexes with metal ions, usually resulting in the deprotonation of the sulphur ligand. To stabilize RSH and H_2S as neutral ligands on a metal ion, class (b) metal ions in low oxidation states are preferred. Adducts of higher oxidation state metal ions with RSH and H_2S might exist in nonpolar solvents, for example, benzene or toluene. However, these ligands are expected to deprotonate in ionizing solvents.

Relative Affinities of Metal Ions for Sulphur

Attempts have been made to derive a relationship between stability of complexes and size/charge of the metal ions.³¹⁻³³

In Irving-Williams^{34,35} correlation, for a given ligand, the stability order of dipositive metal ions follows the pattern $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$. This order is a consequence of the decreasing size of the metal ions and their ligand field effect across the series.

Ahrland, et al.¹⁷ for the first time classified metal ions into two groups: (i) class (a) metal ions which form most stable complexes with the first atom of each group (N, O, F) and (ii) class (b) metal ions which form the most stable complexes with second or subsequent atoms in aqueous solution. They proposed that the affinity of class (b) metal ions for certain donor atoms depends on the availability of electrons in $(n-1)d$ orbitals of the metal for π -bonding. However, the idea of π -bonding between metal and ligand have been a controversial matter.³⁷⁻³⁹ Pearson⁴⁰⁻⁴² has suggested the terms hard and soft to describe the members of class (a) and class (b). The experimental observations suggest that hard acid combine preferentially with hard bases and vice-versa. This behaviour may be attributed to the following points: (I) various degree of ionic and covalent bonding, (II) π -bonding, (III) electron correlation phenomenon, (IV) solvent effect, and (V) van der Waals forces.

A third border line category⁴⁰ exists besides hard and soft acids and bases. Thus, metal ions like Fe(II), Co(II), Ni(II), Cu(II), Zn(II), etc. act as border line acids and

bases like $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , N_2 are border line bases. Within a group of hard or soft, not all have equivalent hardness. Thus, in spite of being in a group of hard acids, more polarizable cesium ion will be somewhat softer than the lithium ion. Presence of polarizable substituents can also affect the behaviour. For example, pyridine is sufficiently softer than ammonia to be considered as border line. Similarly, presence of electron withdrawing substituents can reduce the softness of a site.

Polarization of soft acids and bases has been frequently proposed as a source of affinity between them. Since many soft acids and bases contain a large number of electrons, one might expect an important contribution from such polarization and from London energies. Although there is a little correlation between polarization and the softness of acids or bases, such effects may contribute to significant degree, but they are not the determining factor. One can, however, look at the softness or class (b) behaviour as the off-diagonal element ($H_{ij} - ES_{ij}$) in the secular determinant which is overlooked by electronegativity arguments. It seems all the more probable as many soft-soft interactions involve cations with high ionization energy and anions with low electron affinity where the orbital energies of donor and acceptor species may be quite close leading to an increased contribution from the off diagonal elements.

Klopman^{43,44} used perturbation theory to discuss the interaction of two species in solution. According to his

calculations, if the orbital energies of the donor and the acceptor are very different, the interaction will be essentially ionic (charge controlled) and when two orbital's energies are closely matched the transfer of charge from donor to acceptor (i.e., covalence) becomes more important (Frontier controlled). By considering orbital energies and solvation energies he was able to calculate softness scale for various acids and bases showing fairly good agreement with the Pearson's or Ahrlund's series of hard and soft central atoms: $\text{Al}^{3+} \succ \text{La}^{3+} \succ \text{Be}^{2+} \succ \text{Mg}^{2+} \succ \text{Ca}^{2+} \succ \text{Fe}^{3+} \succ \text{Sr}^{2+} \succ \text{Cr}^{3+} \succ \text{Ba}^{2+} \succ \text{Ga}^{2+} \succ \text{Cr}^{2+} \succ \text{Fe}^{2+} \succ \text{Li}^+ \succ \text{Cu}^{2+} \succ \text{H}^+ \succ \text{Tl}^+ \succ \text{Cd}^{2+} \succ \text{Ag}^+ \succ \text{Tl}^{3+} \succ \text{Au}^+ \succ \text{Hg}^+$. Thus, acids with high oxidation number become relatively softer in nonpolar solvents e.g., Te(IV) coordinates with diarsine, a soft base, in dioxane more strongly than Fe(III) and Cr(III).⁴⁵

Williams and Hale⁴⁶ deplored the quantitative notion of hard and soft acids and bases. They believe that a/b classification is little more than a reflection of σ bonding and the gross controlling factor of the classification is clearly the relative importance of ionic and covalent bonding which has been measured by the value of $\left(\frac{1}{\text{I.P.} \times r_e} \right)$ where I.P. is the ionization potential of acceptor and r_e , the metal ligand bond distance. The higher the value of this function, the higher is the ionic character of the bond. The percentage ionic character, when an acceptor of one type goes over to an acceptor of the other, depends upon the charge, the type of reactants and

the solvent (ligand) bound to them. They further believed that London energies and classical polarization are also important to some extent, but as with π -bonding no quantitative demonstration of these effects has been done.

Drago et al.⁴⁷⁻⁵⁰ have proposed the relationship, $-\Delta H = E_A E_B + C_A C_B$, for the formation of acid-base complexes, where H is the enthalpy of formation of a complex, E_A , C_A and E_B , C_B are the parameters characteristics of acids and bases. In this relationship E and C parameters take account of the electrostatic and covalent interactions respectively. The purpose of E and C parameters is two-fold: (i) it enables predictions to be made concerning the enthalpies of reactions and (ii) it enables to obtain some insight into the nature of the bonding in various systems. Thus, if we compare the C_A and E_A parameters of iodine and phenol, it appears that I_2 is twice as good a covalent bonder as phenol, but that the latter is about five times as effective through the electrostatic attractions.

Ahrland⁵¹ has pointed out that the hard-hard interactions are generally endothermic while the soft-soft interactions are exothermic. Thus, from the above discussion it appears that most probably hard-hard interaction is mostly ionic, while the soft-soft one mostly covalent type which is variable from one system to other.

The nature of M-S bond can also be demonstrated by finding the position of the ligand in nephelauxetic series. The nephelauxetic effect⁵²⁻⁵⁴ to some extent is a measure of covalency in a particular bond formed between the ligand and metal ion. The repulsion between the d electrons which is measured by the numerical value of B (Racah parameter), is decreased by 5-40% after complex formation. The ratio, (B/B^0) , given by the greek letter β , where B^0 and B are the electrostatic repulsion parameter for the metal ions in the gaseous and complexed state respectively, is a measure of covalency in the M-S bond. Thus, if the bond formed between metal and sulphur is highly covalent, the sulphur ligands should have high nephelauxetic effect or low value of β . However, not all sulphur ligands have low value of β . The following series which is in decreasing order of β , contains variable position for sulphur ligand: $F^- > H_2O > RCOO^- > (NH_2)_2CO \approx NH_2CH_2CH_2NH_2 > NCS^- > OH^- > CN^- > SCN^- > Br^- > (C_2H_5O)_2PS_2^- > S^{2-} \approx I^-$. It will be interesting to note that this series follows roughly the order of decreasing electronegativity $F > O > N > Cl > Br > S \approx I$. In the spectrochemical series, given below, the position of the sulphur ligands varies with the type of ligand: $I^- < Br^- < SCN^- < (EtO)_2PSe_2^{2-} \approx S^{2-} \approx (EtO)_2PS_2^- < F^- < Et_2NCS^- < (NH_2)_2CO \approx OH^- < C_2O_4^{2-} \approx O^{2-} \approx H_2O < NCS^- < glycine < Py \approx NH_3 < en \approx SO_3^{2-} \approx NO_2^- < phen \approx bipy < H^- < CH_3 < CN^- < CO$. Probably R_2S occurs between H_2O and NCS^- . As $10 Dq$ is the difference between the σ -antibonding effect on the higher subshell

(e_g in octahedral and t_2 in tetrahedral symmetry) and π -anti-bonding effects on the lower subshell (t_{2g} or e_g respectively). One can rationalize that ligands containing one lone pair, such as H^- , NH_3 , SO_3^{2-} form only σ bonds and have large values of $10 Dq$. On the other hand, ligands with several lone pairs also have π -bonding effect on the partially filled shell of the metal ion and increase in the $10 Dq$ in the order: $(C_2H_5)_2PS_2^- < (C_2H_5)_2NCS_2^- < (C_2H_5)_2OCS_2^-$. This effect has also been observed by Jørgensen in the sulphur containing ligands: $dtf^- < exan < dtc^- < dmp < thioglycolate < dithiomalonate < amines$.

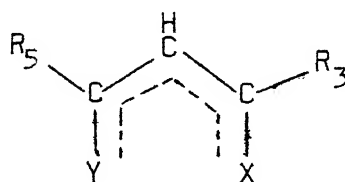
It is obvious from the discussion given in the foregoing paragraphs, that the hard-hard interactions are almost universally accepted to be mainly electrostatic in nature and mostly explanations are given for soft-soft interactions. Increased covalence is generally accepted as an important feature, but the roles of the other factors are still in a confused state which needs more work for clarity of the picture of the M-S bond. Since the present thesis describes the complexing behaviour of ligands containing $-C(S)NHC(O)-$ moieties, the earlier work regarding the complexing behaviours of the ligands having analogous group is briefly described in the following paragraphs.

Complexes of the ligands analogous to the systems studied for the present work

(A) Monothio β -diketones

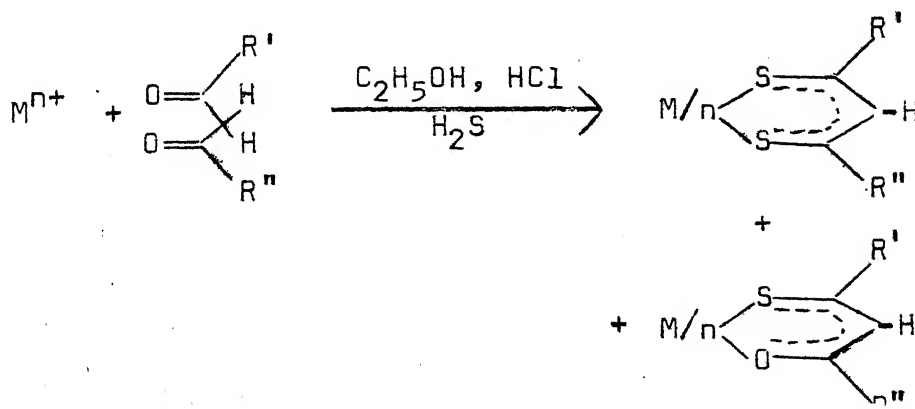
β -Diketones have been extensively used as chelating agents for many years. On substituting oxygen in these ligands by other

donor atoms a set of interesting ligands have^S been obtained whose ligational behaviours were extensively studied. Table I.2 lists a number of such substituted monothioand dithio β -diketones.



$X = O,$	$Y = O$	β -Diketones
$X = O,$	$Y = NR$	β -Ketoamines
$X = O,$	$Y = S$	Monothio- β -diketones
$X = S,$	$Y = NR$	β -Aminothiones.

Although the first attempt to prepare thio- β -diketones was made as early as 1906 by Fromm and Ziersch⁵⁵ who obtained a colourless dimer ($C_{10}H_{16}S_4$) as a result of the reaction of acetylacetone with H_2S in HCl solution, but Martin and Stewart⁵⁶ were successful in synthesizing a number of thio- β -diketone complexes by trapping their monomers by the metal ions in the same reaction before these could dimerise. The general method of preparation of the complexes can be represented by the following equation:



Chelation by thio- β -diketones is achieved with most metals by the direct reactions of metal halides or acetates in suitable solvents. In some cases the presence of a base like triethylamine, pyridine, etc. improved the per cent yields of the products. The metal complexes are unusually deeply coloured, insoluble in water, slightly soluble in alcohols, benzene and easily soluble in chloroform and acetone. Most of the complexes of various monothio ligands along with their references are presented in Table I.3:

Attempts to synthesize monothio β -diketone complexes of V(III) and Cr(II), even in the absence of air, resulted in the formation of those of V(IV) and Cr(III). Both the five and six coordinate complexes of V(IV) are known.^{57,58} The octahedral VO_2L_2 ($LH = C_4H_3SCSH=CHCOF_3$) is dimeric in nitrobenzene, while the complexes of the type $VO_2L'_2$ ($L'H = RCSH=CHCOR'$; $R = Ph$, $R' = Ph$, OEt ; $R = Me$, $R' = Ph$) are monomeric in benzene, are considered to have square pyramidal structure. $Cr(RCS=CHCOR')_3$ ($R = R' = Ph$; $R = Ph$, 2-thienyl, β -naphthyl and $R' = CF_3$) have been synthesized and their structures have been shown to be cis(facial) octahedral. Monothio- β -diketone complexes,⁵⁹ FeL_2 and CoL_2 ($LH =$ thiobenzoylacetone, monothioacetylacetone) have been found to show planar \rightleftharpoons tetrahedral equilibrium in solution. Fe(III) chelates⁶⁰ of $RCSCHCOR'$ ($R = Ph$, $R' = Ph$, Me ; $R = C_4H_3S$, β -naphthyl, $p(m)-XC_6H_4$; $X = Cl$, Br , Me , MeO and $R' = CF_3$) exhibited an anomalous magnetic behaviour. Thus, the metal

ions complexes with $R = \text{Ph}$, $R' = \text{OEt}$ have been found to be in high spin state whereas the magnetic moments of other complexes were temperature dependent because of the presence of thermal equilibrium between the nearly equienergetic spin paired (t_{2g}^5) and spin free ($t_{2g}^3 e_g^2$) configurations of Fe(III) . These equienergetic states have been found to be due to equal magnitudes of the ligand field strength ($10 Dq$) and the pairing energy (P) in them. Further the ligand field strength and consequently the magnetic behaviour were sensitive to R and R' . Apparently electron withdrawing groups appeared to be most effective in increasing the population of spin paired configuration. Cox, et al.⁶¹⁻⁶⁴ obtained the Mossbauer spectral parameters for the four Fe(III) complexes and the results together with the magnetic susceptibility data were interpreted in terms of the thermal equilibrium between sextet 6A_1 and doublet $^2T_{2g}$ states.

Dipolemoments⁶⁵⁻⁶⁹ of $M(\text{RCS}=\text{CHCOR}')_n$ ($M = \text{Pd, Pt, Ni, Cu, Zn}$ when $n = 2$, and Fe, Co, Ru, Rh when $n = 3$) indicated cis(facial) octahedral structures for $M(\text{III})$ complexes and cis square planar for $M(\text{II})$ (Pd, Pt, Ni) complexes. Cu(II) complexes showed slightly lower dipolemoments than the corresponding Pd, Pt and Ni ones.

Structural investigations^{70,71} of $M(\text{PhCS}=\text{CHCOPh})_2$ ($M = \text{Pd, Pt}$) by X-ray have revealed the $M-S$ distances to be 2.26 and 2.22 Å, respectively. The pronounced shortening of Pd-S bond compared to the single bond indicated considerable degree of

Table I.2Monothio and Dithio- β -diketone Ligand Abbreviations[‡]

R_3	R_5	X	Y	Anion Abbreviation
CH_3	CH_3	O	O	acac
CH_3	CH_3	S	O	Sacac
CH_3	CH_3	S	S	SacSac
OC_2H_5	CH_3	O	S	OEt-acSac
OC_2H_5	CH_3	S	S	OEt-SacSac
C_6H_5	CH_3	O	S	Ph-acSac
C_6H_5	C_6H_5	O	S	Ph-acPh-Sac
C_6H_5	C_6H_5	S	S	Ph-SacPh-Sac
NH_2	NH_2	S	S	NH_2 -Sac NH_2 -Sac
OC_2H_5	OC_2H_5	O	S	OEt-acOEt-Sac
$t\text{-C}_4\text{H}_9$	$t\text{-C}_4\text{H}_9$	O	S	Bu^t -ac Bu^t -Sac
$t\text{-C}_4\text{H}_9$	$t\text{-C}_4\text{H}_9$	S	S	Bu^t -Sac Bu^t -Sac
CF_3	CH_3	O	S	CF_3 -acSac
CF_3	CH_3	S	S	CF_3 -SacSac
O-n- C_3H_7	CH_3	S	S	OPr ⁿ -SacSac
Pyrrolidyl	CH_3	S	S	Pyrr-SacSac
$\text{N}(\text{C}_2\text{H}_5)_2$	CH_3	S	S	NEt ₂ -SacSac
Piperidyl	CH_3	S	S	Pip-SacSac
CF_3	C_6H_5	S	S	CF_3 -SacPh-Sac

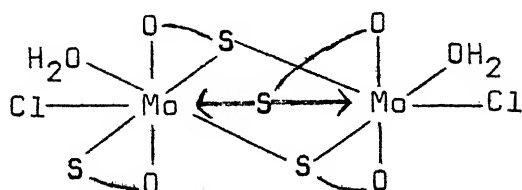
[‡] Taken from Progress in Inorg. Chem., Vol. 27, p. 257.

Table I.3Monothio- β -diketones of Various Metal Ions[‡]

Ligand	Metal Ions	References
PhCSCHCOPh	Ti(IV), V(IV), V(III) Cr(III), Mn(II), Fe(III), Fe(II), Co(III), Co(II), Ni(II), Cu(II), Zn(II), Ru(IV), Ru(III), Rh(III), Pd(II), Ag(I), Cd(II), Os(IV), Os(III), Pt(II), Hg(II), Be(II), Ga(III), In(III), Tl(I), Sn(IV), Sn(II), Bi(III), Pb(II).	93-101
C ₄ H ₃ SCSCHCOCF ₃	V(IV)	102
PhCSCHCOCH ₃	V(III)	103
t-BuCSCHCO-t-Bu	Mn(III)	96
CH ₃ CSCHCOCH ₃	Fe(III), Co(III), Pd(II)	93, 95, 96, 84, 105
CH ₃ CSCHCOPh	Cu(II)	84

[‡]Taken from M. Cox and J. Darken, Coord. Chem. Rev., 7, 29 (1971).

π -bond character in it. $\text{Ni}(\text{acSac})_2$ and its analogs were found to have cis square planar structures.⁷²⁻⁷⁵ Cis(facial) octahedral geometries have been assigned to $\text{Fe}(\text{Ph-acPh-Sac})_3$ ($\mu = 5.50$ BM), $\text{Fe}(\text{Ph-acPh-Sac})_3$ ($\mu = 2.31$ BM)⁷⁶ similar to those of V(III) and Co(III)⁷⁷ complexes. Results showed a marked contraction of the M-X bond lengths in going from high to low spin states. For both the compounds, sulphur atoms lie at the corners of an almost equilateral triangle, denoted as S_3 , parallel to the similar triangle, formed by oxygen atoms, the pairs of plane being separated by 2.60 Å and 2.57 Å for the compounds respectively. The two chelating rings in the tetrahedral complex, $\text{Zn}(\text{OEt-acSac})_2$, did not have equivalent geometries as determined by X-ray method.⁷⁶ Ru(IV) and Os(IV)⁷⁹ → complexes with thiodibenzoylmethane have been shown to be eight coordinate. The diamagnetism of ruthenium complex indicated cubic while the paramagnetism of osmium complex (1.89 BM) an \rightarrow octahedral configuration around the metal ions. Molybdenum(III) complexes⁸⁰ with analogously low magnetic moment (empirical formulae, $\text{Mo}_2\text{L}_4\text{Cl}_2(\text{H}_2\text{O})_3$, where $\text{LH} = \text{RCSH}=\text{CHCOR}'$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Ph}$; OEt ; $\text{R} = 2\text{-thienyl}$, $\text{R} = \text{CF}_3$) have been considered to have eight coordinated tris- μ -thiolobridged structures:



The IR and NMR data of the tetramethylammonium salts⁸¹ of the complex anions $M(CO)_5L^-$ ($M = Cr, Mo, W$; $L^- = RCS=CHCOR$, $R' = R = Ph$; $R = Me, Ph, 2\text{-thienyl}$; $R' = CF_3$) showed the coordination of sulphur with the metal ions. The spectroscopic studies of the polymeric $Cu(I)$, $Ag(I)$, $Cd(II)$, $Hg(II)$ complexes indicated the bonding of the ligand through sulphur.

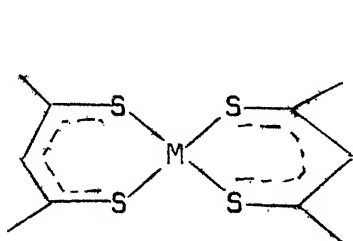
Adducts of $Ni(II)$, $Pd(II)$, $Pt(II)$, $Zn(II)$, $Hg(II)$, $Pb(II)$ complexes of monothio- β -diketones with pyridine, picoline, 2,2'-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline or triphenylphosphine have been synthesized. The adduct of $Ni(II)$ complexes^{82,83} have octahedral geometry, while phenanthroline, bipyridyl and triphenylphosphine adducts of $Pd(II)$ and $Pt(II)$ complexes are four coordinated with metal ions bonded through sulphur. Both five and six coordinated complexes of α and γ -picolines with $Zn(C_4H_3SCS=CHCOCF_3)_2$ have been isolated. $Co(II)$ complexes of thioacetylacetone and monothiodibenzoylmethane⁸⁴ reacted with N-bromosuccinimide to yield the tribromo derivatives, $Co(RCS=CBrcOR)_3$ ($R = Me, Ph$).

The extraction of $Cu(II)$, $Ni(II)$, $Co(II)$ and $Nd(III)$ with monothio- β -diketones have been successfully carried out⁸⁵⁻⁸⁹ at a relatively lower pH. $PhCS=CHCOPh$ has been used for the determination of $Hg(II)$ ⁹⁰ and $Fe(III)$, $Fe(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ ⁹¹ by means of radioisotopic dilution and spectrophotometric methods, respectively. The thin layer chromatographic

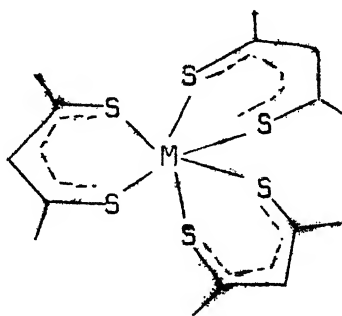
separation⁹² of Fe(III), Co(II), Ni(II), Cu(II), Pd(II), Hg(II), Cd(II), Pb(II) and Zn(II) ions as the chelate of PhCS=CHCOPh has also been successfully achieved.

(B) Dithio- β -diketones

During the past twenty years dithio- β -diketone complexes of a number of bivalent and trivalent metal ions have been synthesized and subjected to detailed physico-chemical studies (Table I.4) which confirmed the dithio- β -diketones to be functioning invariably as bidentate in all the chelates with bonding through thiocarbonyl sulphur atoms and forcing complexes with sufficient electron delocalisation in the chelate rings as represented below:



(M = divalent cation)



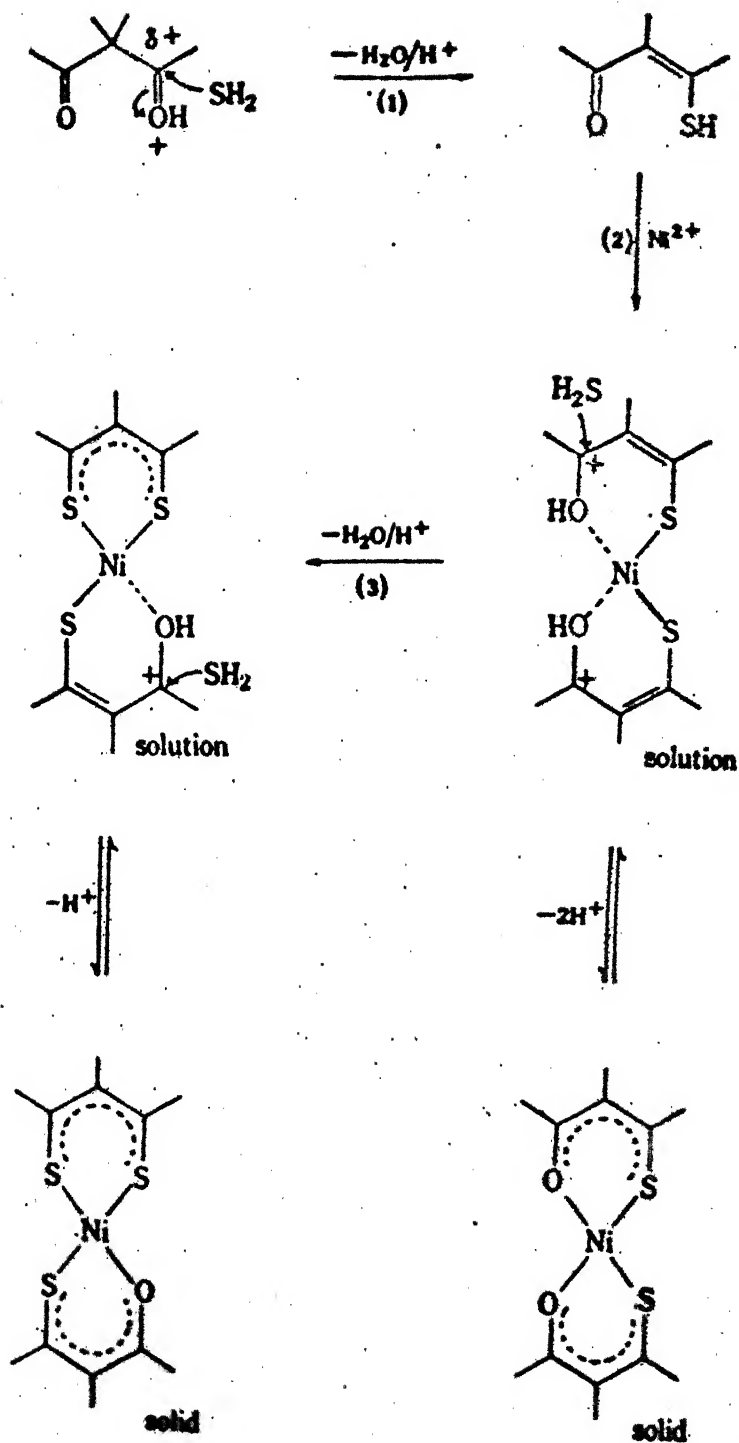
(M = trivalent cation)

The general synthetic procedure of dithio- β -diketones is similar to as described in the earlier parts of the thesis, was due to Martin and Stewart.⁵⁶ The general observations in the preparations of the complexes fit well with the mechanism

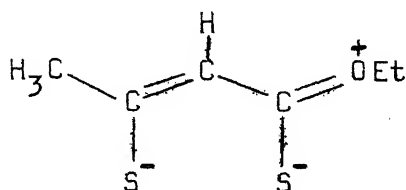
(Scheme 1) exemplified by the reaction of Ni^{2+} with acetylacetone and H_2S in presence of HCl . The complexes were generally highly coloured, stable in air and moisture, insoluble in water but generally soluble in polar organic solvents yielding intensely stable coloured solution with the exception of Fe(III) , Co(III) and Cr(III) ones.

The assignments of the infrared spectral bands of M(SacSac)_2 ($\text{M} = \text{Ni(II)}, \text{Co(II)}$) type of complexes were reported by Ouchi, et al.^{122,127} and Barraclough, et al. which were further substantiated by Siiman and Fresco¹¹⁷ by normal coordinate analysis. They further extended their calculations to include Pd(SacSac)_2 and Pt(SacSac)_2 . Table I.5 lists the principal infrared bands of a variety of dithio- β -diketone metal complexes. The positions of the IR bands were found to be remarkably constant considering the variety of substituents on the chelate ring system. This suggested that the electron delocalisation in the ring is not greatly affected by the presence of electron withdrawing substituents like C_6H_5 and CF_3 . However, a possible exception to this appeared to be the cases of M(OEt-SacSac)_2 ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$), investigated by Hendrickson and Martin¹²⁹ who found significant shift in the position of 700 cm^{-1} band (predominantly $\nu_{\text{C}=\text{S}}$) towards lower wave number and that of 1490 cm^{-1} band (predominantly $\nu_{\text{C}=\text{C}}$) towards higher wave numbers (1510 cm^{-1}). These shifts indicated the change in electron density in the $\text{C}=\text{C}=\text{C}$ backbone

PROPOSED MECHANISM FOR THE FORMATION OF $\text{Ni}(\text{SacSac})_2$



of the chelate ring with a concomitant lowering of the C—S bond order which confirmed the substantial contribution from the canonical form (drawn below), a proposal that is also supported by NMR data of the complexes¹²⁹ and by the properties of the free ligand¹³²:



The assignments proposed¹²⁹ for the IR bands of $\text{Ni}(\text{OEt-SacSac})_2$ were readily transferred to the IR spectral data of the trivalent complexes. Increasing the valency of the central metal ion reduces the frequency at 1510 cm^{-1} ($\nu_{\text{C}=\text{C}}$) to about 1490 cm^{-1} . The positions of all the other bands in the trivalent complexes remained essentially unshifted.

Electron spectra of the complexes of the divalent metal ions (Ni, Pd, Pt) with the ligand SacSac and other similar ligands were discussed mainly by Siiman and Fresco and Martin, et al.^{118,119,129,136} The interpretation of the electronic spectra for trivalent metal ions has been described elsewhere,^{135,140,153} Δ and B parameters were also calculated for these complexes. A general observation is that the spectral data should be cautiously interpreted since the spectrum of square planar $\text{Co}(\text{SacSac})_2$, a paramagnetic d^7 complex is more complicated

than those of d^8 . Since for d^{10} system $[M(OEt-SacSac)_2]$; $M = Zn, Cd, Hg$, the bands due to $L \rightarrow M$ charge transfer and $d-d$ transitions are not possible, the intense transitions must be due to $M \rightarrow L$ and $L \rightarrow L^*$ type only.¹²⁵

The complexes of $Ni(II)$, $Pd(II)$ and $Pt(II)$ were found to be diamagnetic and square planar. The $Cd(II)$ and $Hg(II)$ complexes of $OEt-SacSacH$ were probably isomorphous to the tetrahedral $Zn(II)$ chelate.¹³⁰ Mössbauer¹⁴⁷⁻¹⁴⁹ and ESR^{144,145} studies have been carried out on $Fe(III)$ complex which was found to be low spin similar to those of $Ru(III)$ and $Os(III)$. $Cr(SacSac)_3$ exhibited paramagnetism¹⁵³ equivalent to three unpaired electrons.

These complexes have been subjected to other physical techniques such as NMR, X-ray and Mass spectrometry and the references are cited in Table I.6.

Table I.6

General References for NMR, X-ray and Mass

Technique	References
NMR	106, 123, 125, 129, 140, 155, 157.
X-ray	107, 108, 141, 143, 160, 161.
Mass	118-120, 129, 136.
Magnetic and ESR	23, 111, 158, 159.

Table I.4aDithio- β -diketone Complexes of Bivalent Metal Ions

Ligand	Metal(II)	References
SacSac	Co	56, 106-118
	Ni	56, 106, 108, 109, 117 -122
	Pd, Pt	56, 109, 117, 118, 123
	Zn	124-126
CF ₃ -SacSac	Co	127
	Ni	106, 127
CF ₃ -SacPh-Sac	Ni	119, 127
OMe-SacSac	Ni	120, 128
OEt-SacSac	Co	125
	Ni	120, 129
	Pd, Pt	129
	Zn	130-132
	Cd, Hg	131, 132
Ph-SacSac	Co	133
	Ni	106, 119, 127, 133, 134
	Fe, Zn	134
Ph-SacPh-Sac	Ni	127, 135

...contd.

Table I.4a (contd.)

Ligand	Metal(II)	References
NH ₂ -SacNH ₂ -Sac	Ni, Pd, Pt	136
Bu ^t -SacBu ^t -Sac	Ni	119, 137, 138
Oct ⁿ -SacSac	Ni	119

Table I.4bDithio- β -diketone Complexes of Trivalent Metal Ions

Ligand	Metal(III)	References
SacSac	Co	116, 139, 140
	Rh	140, 142
	Ir	109, 140
	Fe	135, 139, 142-149
	Ru, Os	135, 142, 145
	Cr	139, 153
Ph-SacPh-Sac	Co	150
OEt-SacSac	Co, Rh, Ir	151
	Fe, Ru, Os	

Table I.5

Principal Infrared Bands (cm^{-1}) and Assignments for Complexes
of the type $\text{M}(\text{dithio-}\beta\text{-diketone})_2$

Compound	$\nu_{\text{C}=\text{C}}$ + $\delta_{\text{C-H}}$	$\nu_{\text{C}=\text{C}}$	$\delta_{\text{C-H}}$	$\pi_{\text{C-H}}$	$\nu_{\text{C}=\text{S}}$	$\nu_{\text{M-S}}$	Reference
	2	3	4	5	6	7	
Ni(SacSac) ₂	1491	1344	1312, 1290	830	703	365	106
Pd(SacSac) ₂	1479	1343	1321, 1301	830	705	-	117
Pt(SacSac) ₂	1467	1342	1315, 1300	833	706	-	117
Zn(SacSac) ₂	1489	1341	1321	840	694	363	125
Ni(OEt-SacSac) ₂	1510	1344	1324, 1290	824, 820	639	364	129
Pd(OEt-SacSac) ₂	1509, 1500	1341	1324, 1295	822, 818	639	379	129
Pt(OEt-SacSac) ₂	1508, 1495	1341	1311, 1295	822, 815	637	367	129
Co(Ph-SacSac) ₂	1470	1344	1293, 1270	857	693	-	129
Ni(Ph-SacSac) ₂	1470	1350	1298, 1273	840	690	-	133
Co(CF ₃ -SacSac) ₂	1490	1340	1303	845	695	-	127

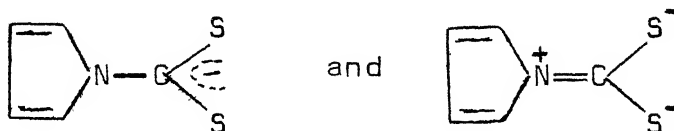
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Table I.5 (contd.)

1	2	3	4	5	6	7	8
Ni(CF ₃ -SacSac) ₂	1490	1340	1302	848	695	-	127
Ni(CF ₃ -SacPh-Sac) ₂	1490	?	1295	850	695	-	127
Ni(Ph-SacPh-Sac) ₂	1471	1347	1295	840	692	-	127

(C) Pyrrole-N-Carbodithiate

Recently^{153,180} a sulphur containing pyrrole derivative, pyrrole-N-carbodithiate^O has been used as a ligand whose properties correspond to the general properties of dithiocarbamate complexes. This ligand is prepared by the direct interaction of CS₂ with pyrrole in DMSO. The anion of the ligand can be represented by the following structures;



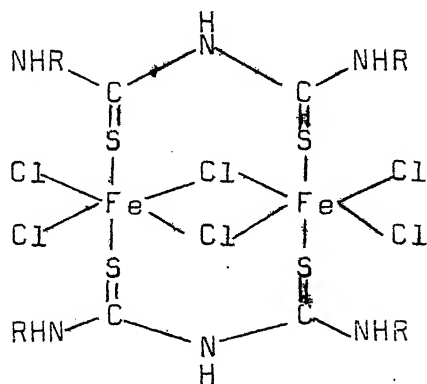
The easy oxidation of Co(II) complex of this ligand is reported to occur unlike the earlier report which says that such ligands are effective in stabilising lower oxidation state,¹⁵² although oxidation of metal ions by such ligands is not unusual.¹⁵⁴

(D) Monothiobiuret

Only few complexes of this ligand have been reported so far. ML₂Cl₂ types of complexes¹⁶² (L = NH₂CONHCSNH₂; M = Co(II), Ni(II), Cd(II), Hg(II)) have been synthesized and their structures have been proposed on the basis of spectral (IR and electronic) and magnetic studies. In Ni(II) and Cd(II) complexes the ligand acted as bidentate, while in tetrahedral Co(II) and Hg(II) complexes as unidentate.

(E) Dithiobiuret ^{163-165, 167-170}

The complexes of Zn(II), Ni(II), Sn(II), Cu(II) with substituted dithiobiuret ($R=R' = \text{Et, Me, morpholine}$)¹⁷¹ have been found to be useful in population control and as insecticides and those of Ag(I), Cu(I), Ni(II), Pd(II), Hg(II), Fe(III), Zn(II), Cd(II), Cu(II) and Co(II)¹⁷²⁻¹⁷⁶ with substituted dithiobiuret ($\text{RNHCSNHCSNHR}'$, $R = \text{Ph}$, $R' = o\text{-MeC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$; $R = \text{Me}$, $R' = o\text{-MeC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$), as fungicides. Tetrahedral structures have been proposed for the complexes, $\text{M(II)(RNHCSNHCSNHR}')$ ₂ ($\text{M} = \text{Zn, Cd, Hg, Co, Ni, Cu, Pd, Sn}$) on the basis of IR, magnetic and conductance studies and the following structure for the Fe(III) complex has been proposed:



A few addition compounds^{78, 104, 168} of $\text{Ni(NH}_2\text{CSNHCSNH}_2)_2\text{X}_2$ ($\text{X} = \text{Cl, Br, I, } \frac{1}{2} \text{SO}_4, \text{CH}_3\text{COO}^-$) have also been isolated. The crystal structures³⁶ of two of the addition compounds, $\text{Ni(NH}_2\text{CSNHCSNH}_2)_2 \cdot \text{glycol}$, $\text{Ni(NH}_2\text{CSNHCSNH}_2)_2(\text{ClO}_4)_2 \cdot \text{EtOH}$ have been determined to investigate (a) the class_(a, or b) of metal-ligand

in the neutral complex, (b) structural differences between neutral ligand complexes and uninegative complex, and (c) the hydrogen bonded system in the cationic complexes. In the cation complex, $[\text{Ni}(\text{NH}_2\text{CSNHCSNH}_2)_2]^{2+}$, the interatomic distances and bond angles were found to be similar to those of neutral complex $\text{Ni}(\text{NH}_2\text{CSNHCSNH}_2)_2$ except that S-C and C-N bonds were respectively shorter and longer, and the S-C-N (terminal) and N(terminal)-C-N(central) bond angles respectively higher and lower than those in the neutral complex. The structure of the complex¹⁶⁶ $\text{Cu(I)}(\text{S}_2\text{C}_2\text{N}_3\text{H}_4)_2\text{Cl}_2$ was described as infinite chain of chloride bridged Cu(I) species and the ligand is bonded to Cu(I) through nitrogen and not through sulphur, although nitrogen is considered a relatively harder base compared to disulphide. Pseudotetrahedral structure has been assigned to the complex, $[\text{Cp}_2\text{V}(\text{NH}_2\text{CSNHCSNH}_2)][\text{PF}_6]$ (Cp = n-cyclopentadienyl) on the basis of IR, magnetic susceptibility, ESR, electronic spectra and molar conductance studies.¹⁷⁷

Gal, et al.¹⁷⁸ have prepared square planar complexes of Rh and Pt, having general formula $\text{Rh}(\text{CO})(\text{PPh}_3)\text{L}$, $\text{Rh}(\text{PPh}_3)_2\text{L}$, $\text{PtH}(\text{PPh}_3)\text{L}$ (L is bidentate, coordinating through S and S, $\text{L} = \text{H}_2\text{NCSNHCSNH}_2$). These compounds undergo reaction with oxygen giving 1:1 dioxygen adduct. In solution trans-product of the complex $\text{Rh}(\text{PPh}_3)_2(\text{O}_2)\text{L}$ has been observed.

(F) N-Ethoxycarbonylpyrrole-2-thiocarboxamide and N-Phenyl-carbamoylpyrrole-2-thiocarboxamide

These ligands¹⁷⁹ can function either as neutral or as anions with N, S and oxygen as potential donors. Obviously their simultaneous participation in the complex formation would virtually be impossible. Thus, monomeric and polymeric complexes have been synthesized with the metal ions: Co(II), Ni(II), Cu(II), Cu(I), Ag(I), Zn(II), Cd(II), Pt(II), Pt(IV), Pd(II), Rh(I), Rh(III), Ru(II), Ru(III) and Au(II). Different modes of bonding have been reported; the ligand as bidentate and bonded through thiocarbonyl sulphur and carbonyl oxygen; acting as unidentate and bonded through thiocarbonyl sulphur; anionic and neutral forms of ligand; acting as bidentate towards two metal ions through N and S atoms or both through nitrogen atoms. The interesting part with this ligand is that they form diamagnetic complexes with Co(II).

In view of the potential interest in the complexing properties of the above mentioned ligands, having S and N as potential donors, it is surprising that relatively few transition metal complexes with pyrrole containing ligands have been studied in detail. With this objective under consideration the complexes of 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide have been studied with various metal ions which have been described in this thesis.

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CHAPTER II

REACTIONS OF 2-THIOPYRROLE-1,2-DICARBOXIMIDE AND N-CARBAMOYL-PYRROLE-2-THIOCARBOXAMIDE WITH THE COMPOUNDS OF Cu(I), Ag(I), Cd(II), Hg(II) and Pb(II)[‡]

This chapter describes the syntheses of Cu(I) and Ag(I) complexes with 2-thiopyrrole-1,2-dicarboximide and N-carbamoyl-pyrrole-2-thiocarboxamide. The behaviour of these two ligands towards Cd(II), Hg(II) and Pb(II) compounds have^S also been studied. The main feature of most of these reactions has been the sulphur abstraction from the ligand by the metal ions other than Cu(I) and thus the oxidation product of the ligands have^S been isolated. The products have been characterised by means

[‡]Indian J. Chem., 20A, 1196 (1981).

of chemical analyses, infrared, electronic spectral and magnetic measurement studies. Their probable structures have been suggested.

EXPERIMENTAL

All the chemicals used were either chemically pure or AnalaR grade. $[\text{Cu}(\text{MPh}_3)_3\text{X}]$, ($\text{M} = \text{P}, \text{As}$; $\text{X} = \text{Cl}, \text{Br}$) was prepared by the literature method.¹

(A) Preparation of the Ligands

The first step in the syntheses of these ligands involved the preparation of ethoxycarbonyl isothiocyanate (SCNCOOEt).^{2,3} Pyrrole was reacted with SCNCOOEt to give N-ethoxycarbonylpyrrole-2-thiocarboxamide⁴ which on reaction with quinoline gave the first ligand, 2-thiopyrrole-1,2-dicarboximide, the subsequent reaction of which with aqueous ammonia yielded the second ligand, N-carbamoylpyrrole-2-thiocarboxamide.⁵ Ligands are referred to as TPH and CPTH respectively hereafter. Synthetic procedures of these compounds are described below:

(i) Ethoxycarbonyl isothiocyanate (SCNCOOEt)

A mixture of 700 ml of dry acetonitrile and 194 g (2.0 mol) of potassium thiocyanate was warmed on a steam bath and treated portionwise with 217 g (2.0 mol) of ethylchloroformate, heating

was continued until the reaction mixture became hot and inorganic precipitate thickened rapidly. At this point the mixture became yellow. The heat source was removed and reaction allowed to run its course. The mixture was permitted to cool slowly at room temperature, chilled and suction filtered. The filtrate was concentrated under reduced pressure and residual oil distilled, yield 162 g, b.p. 51° (13 mm). Redistillation at 10 mm showed that bulk of material distilled at 44°C .

(ii) N-Ethoxycarbonylpyrrole-2-thiocarboxamide (ETH)

A mixture of 16.8 g (0.25 mole) of pyrrole and 32.8 g (0.25 mol) of ethoxycarbonylisothiocyanate, both ice cold, was swirled occasionally and cooled as needed to prevent its temperature from rising above 40°C . Within about an hour the mixture had solidified, whereupon it was allowed to stand overnight. Following repeated washing of the product with petroleum ether (b.p. $60-80^{\circ}\text{C}$), there was obtained 46 g (93%) of N-ethoxycarbonylpyrrole-2-thiocarboxamide, m.p. $95-98^{\circ}\text{C}$. Recrystallization of the product from aqueous ethanol gave the pure compound in the form of yellow crystals, m.p. $98-99^{\circ}\text{C}$.

(iii) 2-Thiopyrrole-1,2-dicarboximide (TPH)

A mixture of 5.0 g of ETH and 15 ml of quinoline was heated in a 25 ml erlenmeyer flask until the temperature of the escaping vapours reached $170-180^{\circ}\text{C}$. The resulting tarry

material was cooled, subsequently mixed with cold, dilute hydrochloric acid and extracted with ether. The ether extract was washed with water, treated with charcoal and dried ^{over} MgSO_4 , ← finally it was evaporated to dryness to yield 3.3 g (87%) of TPH, m.p. 135-138°C. Recrystallisation from aqueous ethanol gave the product in the form of orange crystals, m.p. 140-141°C.

(iv) N-Carbamoylpyrrole-2-thiocarboxamide (CPTH)

A solution of TPH (1 g) in 2 ml of concentrated aqueous ammonia was allowed ^{to stand} for four to five minutes whereupon a precipitate of CPTH was formed which was collected by filtration. The yield of the crude product was 0.80 g (73%) (m.p. 169-170°C). The product was further purified in the form of yellow crystals by recrystallisation from hot water (m.p. 171-172°C).

(B) Preparation of Metal Complexes

(i) Monochloro(2-thiopyrrole-1,2-dicarboximide)copper(I),
 $[\text{Cu}(\text{TPH})\text{Cl}]$

A solution of CuCl in acetonitrile⁶ was slowly added with stirring under nitrogen atmosphere to an ethanolic solution of the ligand (1:2 molar ratio), whereby colour of the solution was changed to dark red. The solution was allowed to stand for about two hours at room temperature which

resulted in the precipitation of a dark brown coloured complex. The product was separated by filtration, washed several times with acetonitrile, ethanol, diethyl ether and dried in vacuo.

The product obtained by using CuBr appeared to be a mixture of the decomposed products.

(ii) Monochloro(2-thiopyrrole-1,2-dicarboximide)bis(triphenylphosphine)copper(I), $[\text{Cu}(\text{PPh}_3)_2(\text{TPH})\text{Cl}]$

25 ml ethanolic solution containing an equivalent amount of TPH (0.16 g, ca. 1.05 mmol) was mixed slowly with 25 ml chloroform or acetonitrile solution of $[\text{Cu}(\text{PPh}_3)_3\text{Cl}]$ (0.9 g, ca. 1 mmol) at room temperature. A dark red coloured solution was obtained immediately. It was refluxed for about half an hour, followed by its concentration at reduced pressure to nearly half the volume. The concentrated solution was allowed to stand for about an hour, whereby dark red crystals were separated out (m.p. 187°C). These were filtered, washed several times with ethanol, solvent ether and dried in vacuo.

The same compound was obtained when the reaction was carried out using CuCl, PPh_3 and TPH as the starting materials. The compound was recrystallised from chloroform and ethanol.

(iii) Attempts to prepare Monobromo(2-thiopyrrole-1,2-dicarboximide)bis(triphenylphosphine)copper(I), $[\text{Cu}(\text{PPh}_3)_2\text{Br}(\text{TPH})]$

The reaction was carried by the procedure similar to

that given in B(ii) except that $[\text{Cu}(\text{PPh}_3)_3\text{Br}]$ was taken in place of $[\text{Cu}(\text{PPh}_3)_3\text{Cl}]$. The compound obtained was of white colour with composition $[\text{Cu}(\text{PPh}_3)_2\text{Br}]$ (m.p. 173°C). Similarly, substituting triphenylphosphine by triphenylarsine a compound having composition $[\text{Cu}(\text{AsPh}_3)_2\text{Br}]$ (m.p. 157°C) was formed.

(iv) N-Carbamoylpyrrole-2-thiocarboxamidate copper(I), $[\text{Cu}(\text{CPT})]$

25 ml of an ammoniacal solution of CuCl (0.10 g, ca. 1 mmol) was treated with 25 ml ethanolic solution of the ligand (0.34 g, ca. 2 mmol) with stirring under nitrogen atmosphere for about half an hour, whereby a green compound was formed which was separated by centrifuging it, washed several times with ammoniacal water, ethanol, diethyl ether and dried in vacuo. The greenish yellow compound was stable upto 200°C and insoluble in most of the organic solvents.

(v) Reactions of TPH with Ag(I) : Preparation of $[\text{Ag}(\text{TP})]$ and $(\text{TPH})^{\text{I}}$

(a) 50 ml of an aqueous cold solution of AgNO_3 (0.17 g, ca. 1 mmol) was treated with 15 ml cold ethanol solution of TPH (\sim 1 mmol), whereby a yellow precipitate was formed which was separated by filtration. It was washed several times with water, ethanol, diethyl ether and dried in vacuo.

(b) The complex was found to be insoluble in all the organic solvents. It was observed that its colour was changed

to black on keeping it for a few days. On refluxing the complex for about half an hour in an ethanol-water solvent, a black precipitate of Ag_2S settled down at the bottom of the flask. It was separated by filtration, washed with water, ethanol and dried in vacuo and analyzed for sulphur and silver. The filtrate after separating the black precipitate was slowly evaporated to near dryness on a water bath. The residue was extracted from dichloromethane. On concentration the extract, an organic compound, $[\text{TPH}']$, in which sulphur atom in $[\text{TPH}]$ was substituted by oxygen, was crystallised out.

(vi) Reactions of CPTH with Ag(I) : Preparation of $[\text{Ag(CPT)}]$ and $(\text{CPTH})'$

The procedure for preparation of these compounds ^{was} ~~were~~ ← similar to those given for the syntheses of $[\text{Ag(TP)}]$ and $(\text{TPH})'$ in B(V) except that CPTH was used in place of TPH. The isolated compounds were $[\text{Ag(CPT)}]$ and $(\text{CPTH})'$.

(vii) Reactions of TPH with Cd(II) , Hg(II) and Pb(II) salts: Preparation of $(\text{TPH})'$

The reactions were carried out by exactly the same procedure as given in B(V) except that the salts of the corresponding metal ions were taken in place of AgNO_3 . The following observations were recorded during the course of reactions:

(a) Cd(II) salt reacted with (TPH) by heating the reaction mixture slowly on a water-bath to give a yellow compound which was found to be a mixture of various compounds. However, when the same mixture was refluxed for a few hours, it gave pure cadmium sulphide in the form of bright yellow precipitate.

(b) The reaction with lead salt gave an immediate black precipitate of PbS.

(c) The salts of Hg(II) reacted with the ligand in presence of sodium acetate to give first a yellow compound which changed into a black compound on keeping it for about a week.

In all the reactions the final product was extracted with dichloromethane and the extract was dried to give a pale yellow organic compound which was characterised as (TPH)' by analytical, mixed melting point and IR data.

(viii) Reactions of CPTH with Cd(II), Hg(II) and Pb(II) salts:
Preparation of (CPTH)'

These reactions were carried out by the methods similar to those described in B(vii). In every reaction the observations were the same as those given in B(vii). The final product was identified as (CPTH)'.

ANALYSES

Estimation of copper and other metal ions (in the absence of phosphines)

A weighed amount of complex was decomposed by digesting it with concentrated HNO_3 for several times until the residue, when taken in water, gave a transparent solution. It was filtered and the filtrate was made neutral if necessary, by repeated evaporation with water and the residue was dissolved in water. Copper was estimated as $[\text{Cu}(\text{en})_2][\text{HgI}_4]$. Silver, cadmium, mercury and lead were estimated as AgCl , $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2$, $[\text{Cu}(\text{en})_2][\text{HgI}_4]$ and PbSO_4 , respectively⁸ in the filtrate obtained after digesting complexes with concentrated nitric acid.

In the phosphine and arsine complexes, the decomposition of the sample was carried out as follows: A weighed amount of the sample was heated with fusion mixture in a parr-bomb. The residue was treated with concentrated H_2SO_4 in a beaker and heated until SO_3 fumes ceased to come out, concentrated HNO_3 was added to it and the solution was evaporated to almost dryness. The treatment with HNO_3 was repeated a number of times until the solution became transparent. Excess of HNO_3 was removed by evaporating it with concentrated HCl and finally HCl was removed by evaporating it with water. Copper was estimated as $[\text{Cu}(\text{en})_2][\text{HgI}_4]$ in the neutral aqueous solution.

Estimation of phosphorus⁹

Samples were decomposed with a fusing mixture (Na_2O_2 , sugar and NaNO_3 in the ratio 20:1:3 in a parr-bomb). The melt was extracted with water and heated to SO_3 fumes after adding concentrated H_2SO_4 . It was diluted with water and filtered if necessary. In the filtrate phosphorus was estimated as ammonium phosphomolybdate.

Estimation of halide and sulphur

For the estimations of halide and sulphur, the complexes were decomposed by fusing a weighed amount of complex with NaNO_3 and NaOH (8 and 64 times ^{the weight} of the sample respectively) ← in a nickel crucible for about 10 minutes. After cooling the crucible and extracting the residue with water, the solution was filtered, neutralised with dilute HNO_3 (in case of halide) or dilute HCl (in case of sulphate). Halides were estimated as AgX and sulphur, as BaSO_4 in the resulting solution.

Carbon, hydrogen and nitrogen were analysed by the Microanalytical Section of the Indian Institute of Technology, Kanpur. The analytical data are presented in Table II.1.

Infrared Spectra

IR spectra of the ligands and the metal complexes were recorded with a Perkin-Elmer 580 Diffraction Grating Infrared Spectrophotometer in the range $4000\text{--}200\text{ cm}^{-1}$. Samples were

prepared as KBr pellets. The major bands of the IR spectra of the ligands are given in Table II.2.

UV-Visible Spectra

The absorption spectra of the ligands were recorded in various solvents (H_2O , EtOH, CHCl_3) and those of the complexes, in chloroform in the region 700-200 nm on a Cary model-17D UV-visible spectrophotometer.

Magnetic Susceptibility Measurements

Magnetic susceptibilities of the complexes were determined with the help of a Gouy balance at room temperature. All the complexes were found to be diamagnetic.

Melting Points

Melting points of the products were determined on Fischer-John melting point apparatus and are uncorrected.

RESULTS AND DISCUSSION

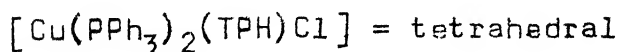
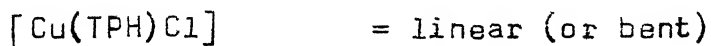
The infrared spectra of the ligands⁵ showed a very complex pattern of bands. However, the spectra were partially analysed to get some information regarding the mode of bonding of metal ions with the ligands. The characteristic bands of pyrrole moiety,¹⁰ present in the ligands' spectra, did not shift

in the spectra of the complexes, (maximum shift $\pm 5 \text{ cm}^{-1}$). This indicated the non-involvement of nitrogen atom of the pyrrole ring in the bond formation. This is also in conformity with the following facts: (1) The nitrogen on the pyrrole ring is poorly basic due to delocalisation of the lone pair of electrons on the nitrogen atom.¹¹ (2) The deprotonation of pyrrole NH group can take place only in the highly basic medium in which ligand is not stable. It was, therefore, assumed that bonding in complexes took place with $-\text{C}(\text{S})\text{NHC}(\text{O})-$ moiety of the ligands and the major shift in the positions of their bands should be in those of thioamide and amide ones.

Cu(I) Complexes of TPH

$[\text{Cu}(\text{TPH})\text{X}]$ and $[\text{Cu}(\text{MPh}_3)_2(\text{TPH})\text{X}]$ ($\text{M} = \text{P}, \text{As}; \text{X} = \text{Cl}^-, \text{Br}^-$) exhibited all the characteristic bands of the ligand and triphenylphosphine or triphenylarsine.¹² In the spectra of the complexes, the following shifts were observed: (a) The position of the amide band I due to $\nu_{\text{C=O}}$ (1765 cm^{-1}) in the ligand shifted to higher wavenumbers ($\Delta\nu$, 25 cm^{-1}) in the complexes, (b) The positions of weak bands at 690 and 620 cm^{-1} assigned to τ_{NH} , did not shift. (c) There were no systematic shifts in the positions of the thioamide, $-\text{N}=\text{C}=\text{S}$, band (II) and (III) and amide bands (II) and (III) in the region $1550-1200 \text{ cm}^{-1}$. Since these bands arise due to the vibrational modes having contributions from $\nu(\text{CN})$, $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{S})$, in the complexes

the mixing pattern will be different from those in the ligand and ~~X~~hence one should expect nonsystematic shifts in the positions of these bands. (d) The thioamide band (IV),¹³ which contains major contribution from $\nu(\text{C}=\text{S})$ appeared around 850 cm^{-1} in the spectra of the ligands. Their positions remained almost stationary suggesting that the thiocarbonyl sulphur did not possibly take part in the bonding. (e) A new band appeared in the spectra of the complexes at around 485 cm^{-1} which was assigned to $\nu(\text{M}-\text{N})$.¹⁴ (f) The position of the broad band around 3200 cm^{-1} did not show any shift in the spectra of the complexes suggesting that the ligands are bonded in the complexes as unprotonated ones. Further, the diamagnetism of all the complexes indicated the oxidation state of copper as +1. Thus, these shifts together with the diamagnetism of the complexes can be explained if the bonding is assumed through N of $-\text{C}(\text{S})\text{NHC}(\text{O})-$ moiety of the ligands. The following tentative geometries to the complexes may then be assigned,



The reactions of $(\text{AsPh}_3)_3\text{CuCl}$ with the ligands TPH or CPTH led to the formation of the decomposed products. It is interesting to note that a similar reaction with boron hydride anions led to an unstable product as observed by Lippard et al.¹ Bromide ion was also found to destabilise the complex.

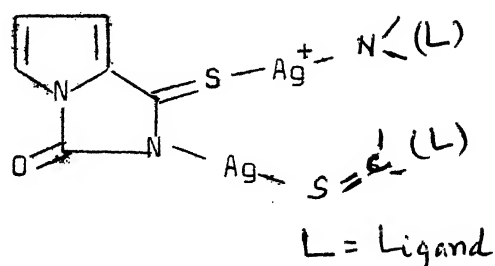
Cu(I) Complex of CPTH

The reaction of CuCl with CPTH, which was carried out in aqueous NH_3 under nitrogen atmosphere yielded a compound, Cu(CPT). The charge balance suggested that the ligand molecule must have deprotonated before forming the complex. The deprotonation of $-\text{C}(\text{S})\text{NHC}(\text{O})-$ moiety was further confirmed from the infrared spectrum of the complex. In the spectrum of the ligand there appeared three bands around 3400 cm^{-1} , 3370 cm^{-1} and 3250 cm^{-1} assigned to $\nu(\text{NH})$. In the spectrum of the complex, however, the band at 3250 cm^{-1} disappeared and a new band around 3160 cm^{-1} appeared. Further, thioamide band (IV) did not shift in the spectrum of the complex. A new band appeared at around 540 cm^{-1} which was assigned to $\nu(\text{M-N})$. These observations suggested that metal ion is bonded through N of $-\text{N-C=S}$ group of the ligand after deprotonation.

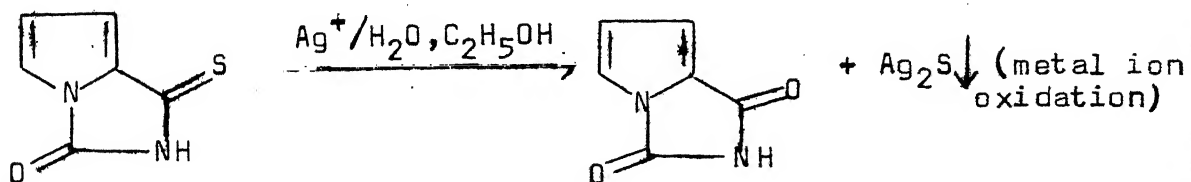
Ag(I), Cd(II), Hg(II) and Pb(II) Complexes of TPH and CPTH

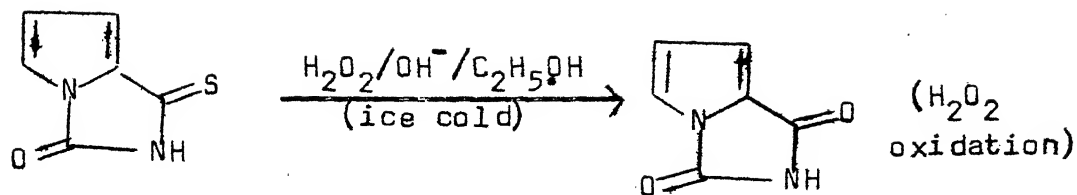
Reactions of the salts of soft metal ions with the two ligands immediately yielded yellow compounds. These compounds were not stable. Therefore, none except those of silver with the formula Ag(TP) and Ag(CPT) have been characterised. In the IR spectra of the silver complexes, the ligand band around 3200 cm^{-1} did not appear. Instead a new band at 3140 cm^{-1} was present. Further, the position of the band due to $\nu(\text{C=O})$ remained stationary in the spectra of the complexes, but the

thioamide band (IV) shifted to lower wavenumber side ($\Delta\nu$ 15 cm^{-1}). Two new bands around 380 cm^{-1} and 550 cm^{-1} assigned to $\nu(\text{M-S})$ and $\nu(\text{M-N})$, respectively appeared in the spectra of the complexes. These shifts can be explained if the following bonding scheme is assumed:

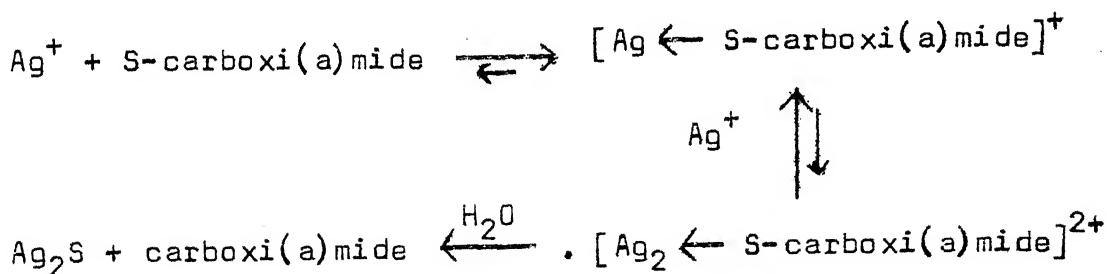


The insolubility of these complexes in most of the solvents indicated their polymeric nature. The silver complexes, on keeping or refluxing formed silver sulphide and the oxidation products of the ligands [(TPH)' and (CPTH)']. The oxidized products have been characterised by mixed melting points and comparing the analytical and IR data of the authentic samples.⁷ The desulfurisation of these ligands by soft metal ions is, however, well known¹⁵ which occurs because of the high polarizing power and high polarizability of the metal ions and soft donors, respectively.¹⁶ This oxidation of ligand by metal ions can be compared with the already existing⁷ method in the following way:





Recently, a mechanism¹⁷ of sulphur uptake by the metal ions such as Hg^{2+} , Ag^+ and Tl^{3+} from S-acetals to form metal sulphides and the corresponding ketones in water-dioxan or water-ethanol solvent has been proposed. In case similar mechanism is assumed in our systems too, the following mechanism may be proposed (exemplified by taking Ag^+);



In cases of $\text{Hg}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ because of the instabilities of the complexes, they could not be isolated in the pure state. The analyses of the precipitated products suggested them to be a mixture of metal-sulphides, oxidized and unoxidized ligands. However, on refluxing the metal ions for a few hours with the ligands in the reaction medium, corresponding pure oxidized product of the ligands along with the precipitated metal sulphides were obtained. These have been characterised by their elemental analyses, mixed melting points and IR spectra.

Reactions of these thiocarboxi(a)mide with the soft metal ions thus provide an alternate route for the preparation of the corresponding carboxi(a)mide.

Electronic spectrum of chloroform solution of the ligand (TPH) exhibited bands at 27000, 30303, 35088 and 36363 cm^{-1} . The band at 30303 cm^{-1} may be due to thiocarbonyl group of the isothiocyanate.¹⁸ Usually transition involving N and S occur in lower energy region (27000, 30303 cm^{-1}) and are relatively less intense than $\pi \rightarrow \pi^*$ transitions.¹⁹ The other two bands may be thus assigned to the intraligand charge transfer bands. The spectrum of the complex $[\text{Cu}(\text{TPH})_2(\text{PPh}_3)_2\text{Cl}]$ in CHCl_3 exhibited bands at 27400(w) cm^{-1} , 30030(s) cm^{-1} , 37000(s) cm^{-1} and 41700 cm^{-1} . A comparison of the band positions of the ligands and those of the complexes showed that the additional bands may be due to the metal to ligand charge transfer since they occur at high energy side²⁰ possibly transfer of metal d electron density to the higher empty molecular orbitals of the ligand is taking place. No d-d bands were observed as expected for the Cu(I) complexes.

Table II.1

Analytical Data of the Complexes

Complexes	Colour	ANALYSES - Found (Calcd) %						
		C	H	N	S	X	P	M
Cu(TPH)Cl	Dark brown	28.3 (28.4)	1.5 (1.6)	11.3 (11.2)	12.9 (12.7)	13.9 (14.1)	-	24.8 (24.5)
Cu(PPH ₃) ₂ (TPH)Cl	Dark red	65.4 (65.1)	4.1 (4.3)	3.6 (3.6)	3.9 (4.1)	4.7 (4.6)	8.1 (8.0)	7.9 (8.1)
Cu(CPT)	Greenish yellow	30.9 (31.2)	2.5 (2.6)	18.4 (18.2)	13.6 (13.8)	-	-	27.3 (27.5)
Ag(TP)	Yellow	27.7 (27.5)	1.6 (1.6)	10.7 (10.8)	12.1 (12.3)	-	-	41.0 (41.1)
Ag(CPT)	Yellow	26.2 (26.1)	2.1 (2.2)	15.4 (15.2)	11.4 (11.5)	-	-	36.4 (36.6)
(TPH)'	Pale yellow	53.1 (52.9)	2.8 (2.9)	20.4 (20.6)				
(CPTH)'	Pale yellow	47.2 (47.1)	4.5 (4.6)	27.2 (27.4)				

Table II.2

Major IR Band Assignments of the Ligands

Ligands (cm^{-1})		Assignments
(TPH)	(CPTH)	
3200	3400, 3370, 3250	$\nu(\text{NH})$
1765	1730	Amide band I, major contributions from $\nu(\text{C=O})$
1560	1570, 1530	Thioamide band I + amide band II
1445, 1405	1475, 1450, 1425	Pyrrole ring vibrations
1350, 1310, 1250, 1230, 1190	1380, 1325, 1270	Thioamide band II + amide band III
1140	1120	Thioamide band III
850	845	Thioamide band IV having major contribution from $\nu(\text{C=S})$
690, 620	705, 640	$\tau(\text{NH})$

Table II.3

UV-Visible Absorption Bands of Ligands
and the Complex (cm^{-1})

Compounds	Solvent	Band position (λ_{max})	Assignment
TPH	CHCl_3	27000	$n \rightarrow \pi^*$
		30303	$\pi \rightarrow \pi^*$
		35088	C.T.
		36363	C.T.
	H_2O	28571	$\pi \rightarrow \pi^*$
		35088	C.T.
	$\text{C}_2\text{H}_5\text{OH}$	30303	$\pi \rightarrow \pi^*$
		35088	C.T.
		36363	C.T.
CPTH	CHCl_3	28570	$\pi \rightarrow \pi^*$
		34483	C.T.
	H_2O	28170	$\pi \rightarrow \pi^*$
		35088	C.T.
	$\text{C}_2\text{H}_5\text{OH}$	28570	$\pi \rightarrow \pi^*$
		35088	C.T.
$[\text{Cu}(\text{PPh}_3)_2(\text{TPH})\text{Cl}]$	CHCl_3	27400	$n \rightarrow \pi^*$
		30030	$\pi \rightarrow \pi^*$
		37000	C.T.
		41700	$M \rightarrow L^*$

LEGEND TO THE FIGURES

Fig. II.1 Infrared Spectra

1. TPH, 2-Thiopyrrole-1,2-dicarboximide
2. CPTH, N-Carbamoylpyrrole-2-thiocarboxamide
3. TPH
4. (TPH)¹, 2-Pyrrole-1,2-dicarboximide
5. Cu(CPT)
6. [Cu(PPh₃)₂(TPH)Cl]

Fig. II.2 UV-Visible Spectra

- A. TPH (H₂O)
- B. TPH (C₂H₅OH)
- C. TPH (CHCl₃)
- D. CPTH (H₂O)
- E. CPTH (C₂H₅OH)
- F. CPTH (CHCl₃)
- G. [Cu(PPh₃)₂(TPH)Cl]

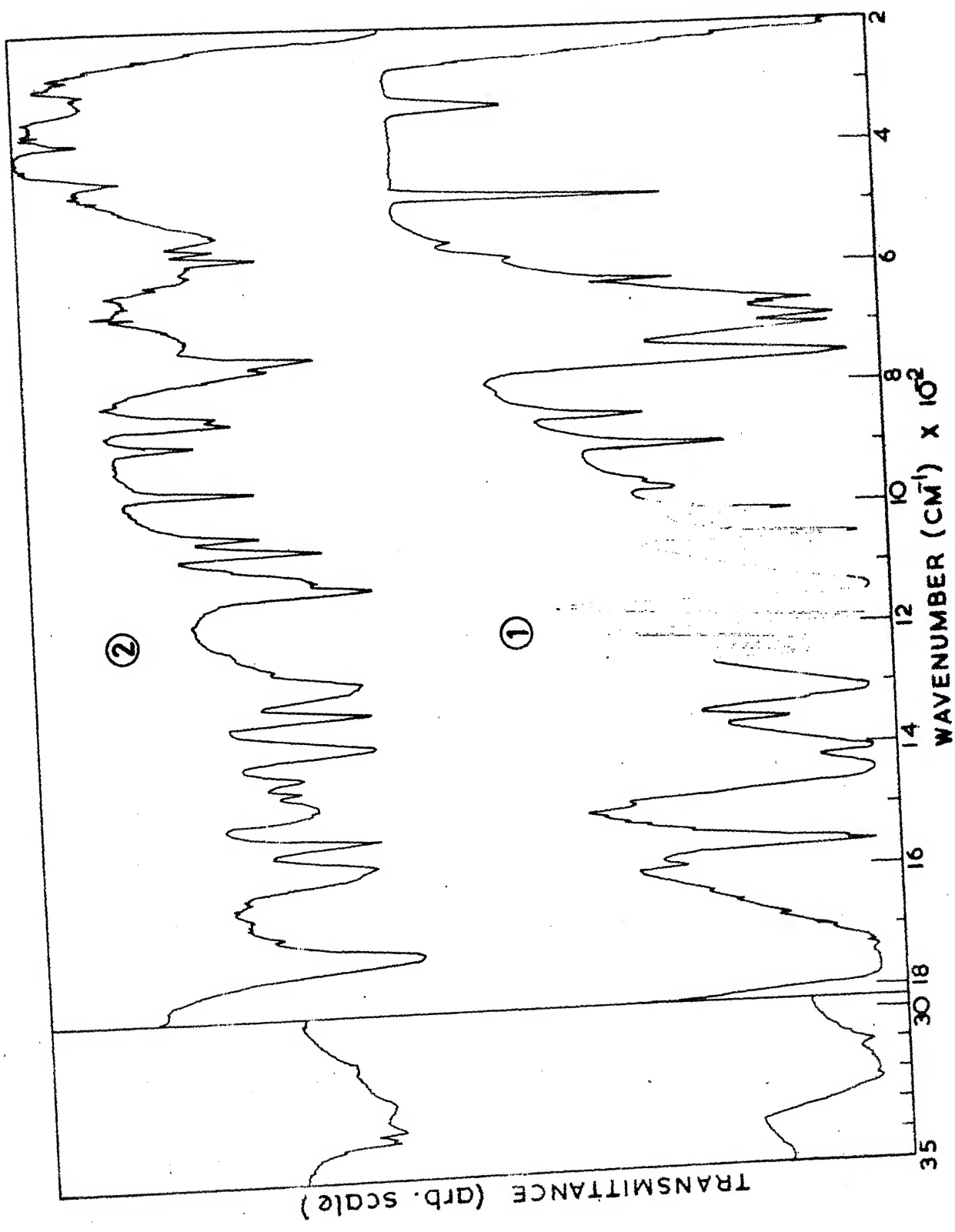


FIG. II.1

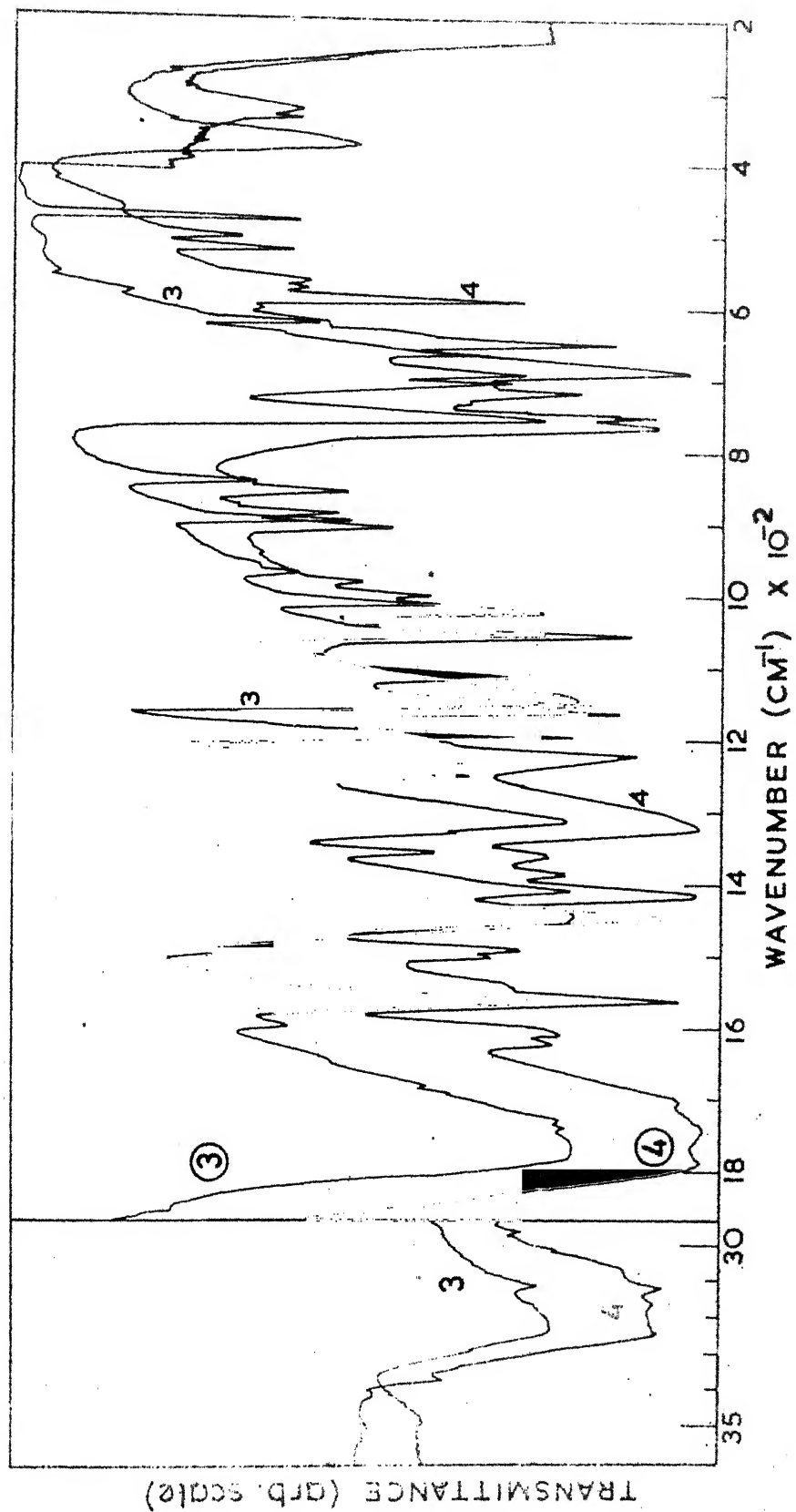


FIG. II.1

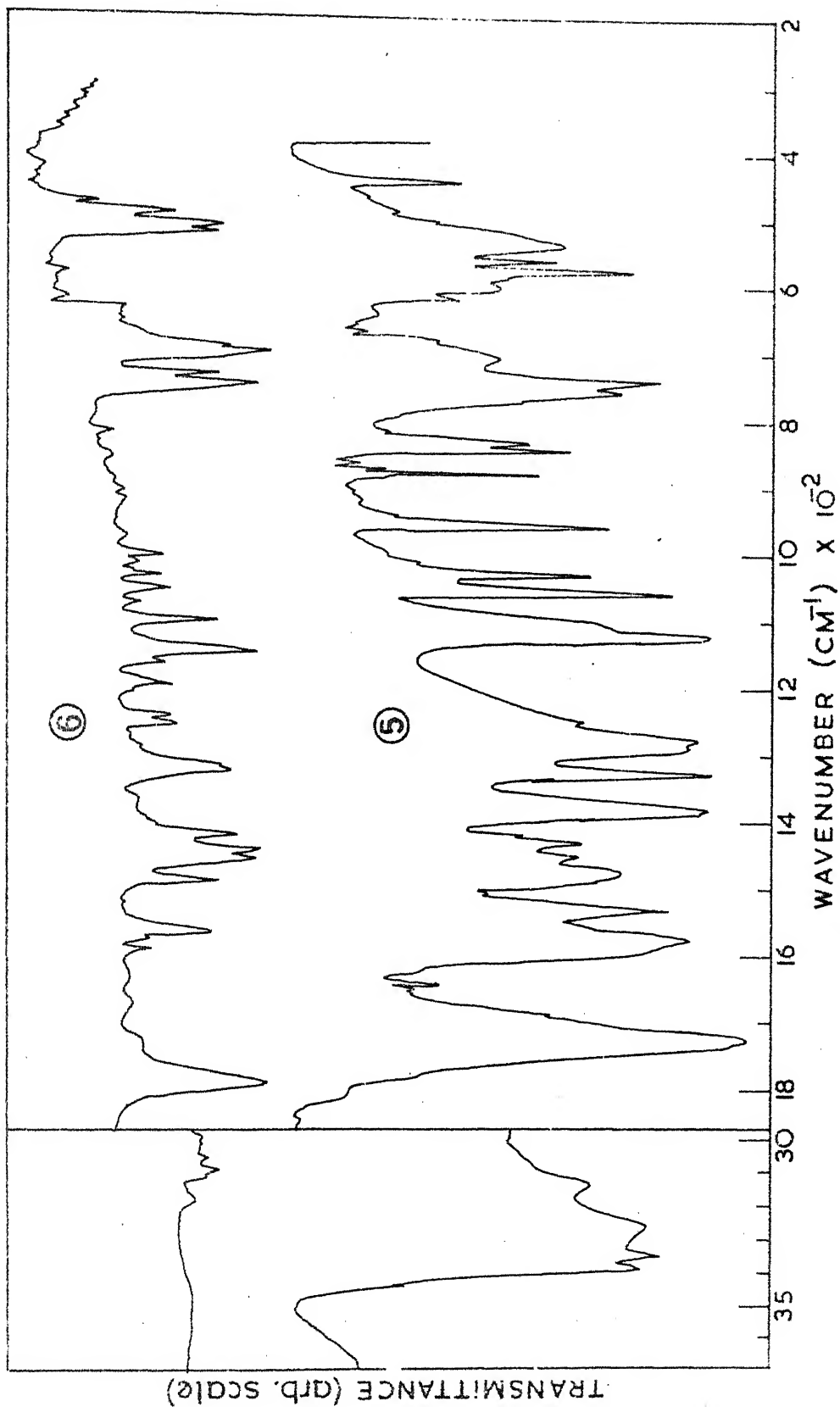


FIG. II.1

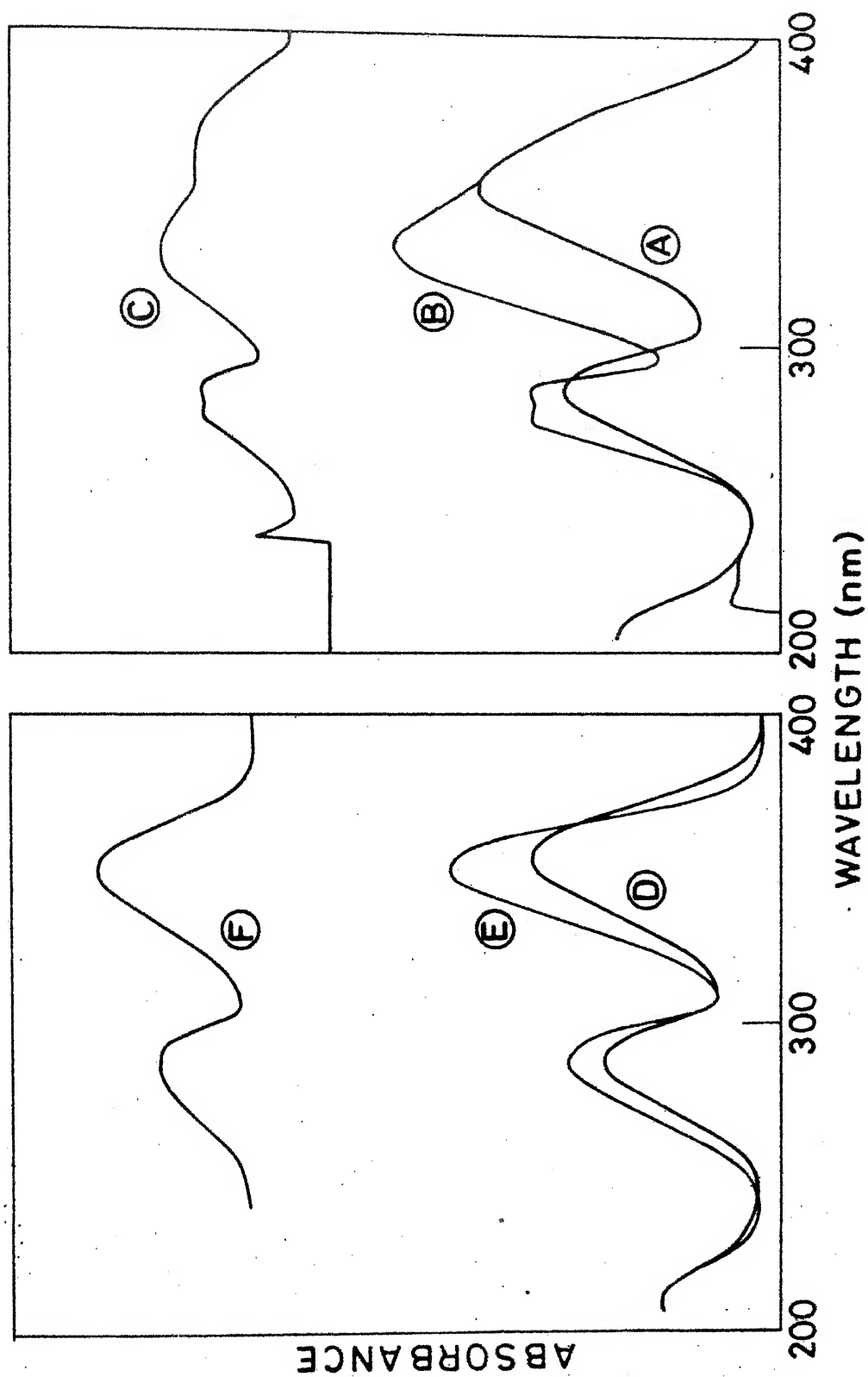


FIG. II.2

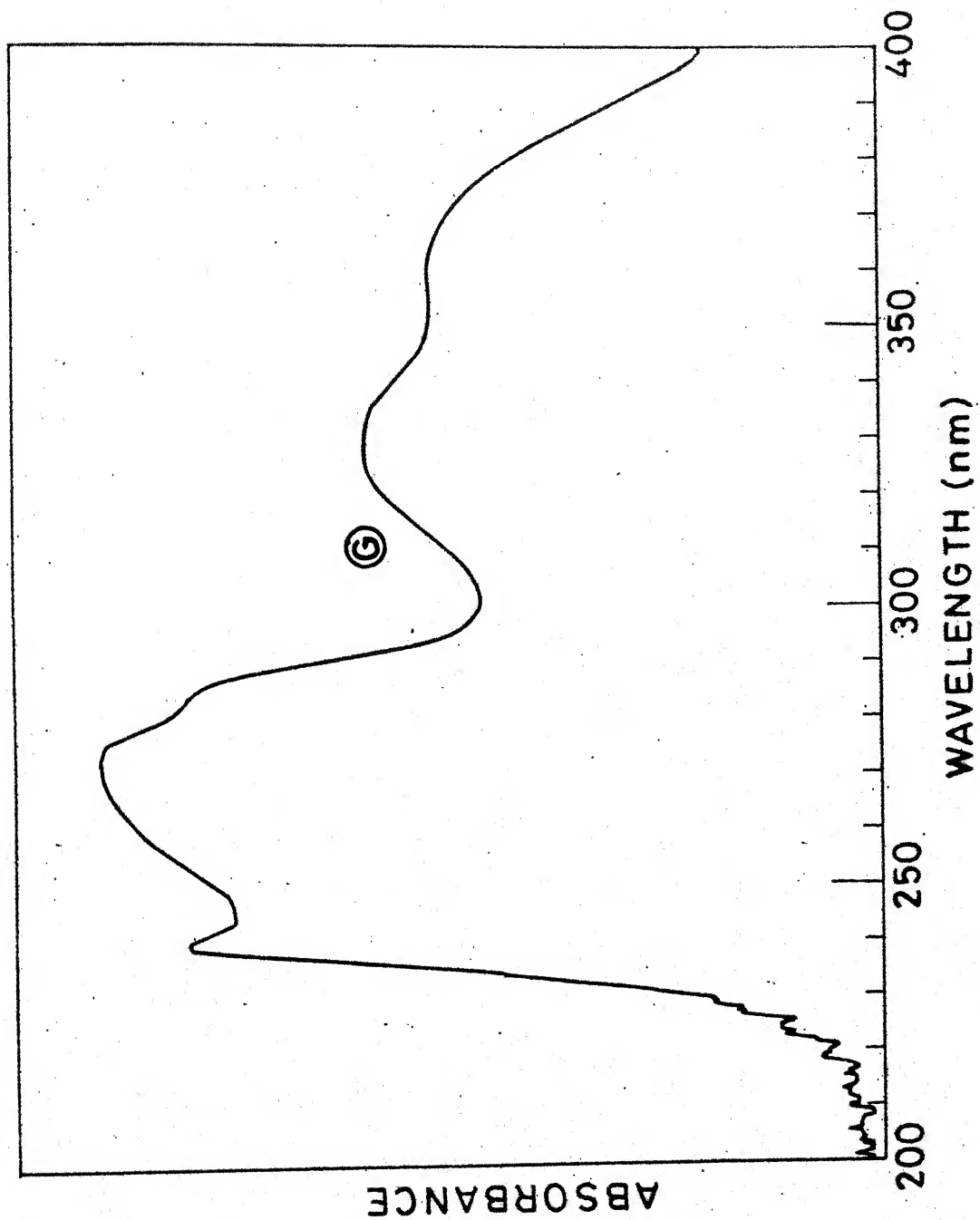


FIG. II.2

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CHAPTER III

UNUSUAL DIAMAGNETIC COBALT(II) COMPLEXES of 2-THIOPYRROLE-1,2-DICARBOXIMIDE AND N-CARBAMOYLPYRROLE-2-THIOCARBOXAMIDE[‡]

This chapter describes the reactions of 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH) with the salts of cobalt(II) and cobalt(III) in presence of several nitrogen bases (pyridine, picolines and imidazole). These reactions led to the formation of less known¹⁻⁵ Co(II) diamagnetic and Co(II) paramagnetic complexes of the type: $[\text{Co}(\text{TP})_2\text{B}]_2$, $[\text{Co}(\text{CPT})_2\text{B}]_2$, $[\text{Co}(\text{CPT})_2]_2$ and $[\text{Co}(\text{TP})_2]$, $[\text{Co}(\text{Py})_4\text{Cl}_2]$, respectively. The complexes, thus obtained, have been subjected to the chemical analyses, infrared and electronic spectral, magnetic measurement and DTA studies

[‡] Indian J. Chem. (in press).

in order to determine the stereochemistries and tentative structures.

EXPERIMENTAL

The chemicals used were either chemically pure or Analytical grade. Ligands were prepared by the methods described in Chapter II and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{en})_3]\text{Cl}_3$ by the literature methods.^{6,7} All the solvents were dried and distilled before use.

Preparation of Metal Complexes

(i) Tetrakis(N-carbamoylpyrrole-2-thiocarboxamidato)dnicobaltate, $[\text{Co}(\text{CPT})_2]_2$

An aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (25 ml) was treated with a few drops of pyridine followed by the addition of 25 ml solution of CPTH in hot water in 1:2 molar ratio. The resulting mixture was refluxed for about half an hour, whereby a reddish brown precipitate settled down. It was separated by centrifugation and washed with hot water. The complex thus obtained was dissolved in the minimum quantity of ethanol and excess of water was added to it whereupon reddish brown precipitate reappeared. The suspension was digested on a water bath and the precipitate was filtered, washed with hot water and dried in vacuo over CaCl_2 . The complex was analysed as $[\text{Co}(\text{CPT})_2]$.

(ii) Bis(2-thiopyrrole-1,2-dicarboximidato)cobalt(II) dihydrate,
 $[\text{Co}(\text{TP})_2] \cdot 2\text{H}_2\text{O}$

An equivalent amount of an aqueous solution of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was treated with an ethanolic solution of the ligand. The mixture was refluxed on a water bath for about two hours, whereby a black brown precipitate was formed. It was filtered, washed several times with water, small amounts of ethanol, finally with diethyl ether, and dried in vacuo. The complex was analysed as $[\text{Co}(\text{TP})_2] \cdot 2\text{H}_2\text{O}$.

(iii) Bispyridinetetrakis(2-thiopyrrole-1,2-dicarboximidato)-
dicobalt(II) tetrahydrate, $[\text{Co}(\text{TP})_2\text{Py}]_2 \cdot 4\text{H}_2\text{O}$

25 ml ethanolic solution containing an equivalent amount of TPH (0.32 g, ca. 2.1 mmol) was mixed with 25 ml of an aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (0.28 g, 1 mmol) at room temperature, followed by the addition of 2 ml of pyridine. The resulting mixture was refluxed for about 1 hour on a water bath, whereby a black-brown complex was precipitated out. It was separated by centrifugation, washed several times with water, small amounts of ethanol, diethylether and dried in vacuo.

(iv) Bis(β -picoline)tetrakis(2-thiopyrrole-1,2-dicarboximato)-
dicobalt(II), $[\text{Co}(\text{TP})_2(\beta\text{-pic})]_2$

The complex was prepared by the procedure given in (iii) except that β -picoline was used in place of pyridine, whereupon a

reddish brown complex was obtained.

(v) Bis(γ -picoline)tetrakis(2-thiopyrrole-1,2-dicarboximidato)-dicobalt(II), $[\text{Co}(\text{TP})_2(\gamma\text{-pic})]_2$

The reddish brown complex was obtained by the procedure similar to that given in (iii) except that γ -picoline was used in place of pyridine.

(vi) Bis(imidazole)tetrakis(2-thiopyrrole-1,2-dicarboximidato)-dicobalt(II), $[\text{Co}(\text{TP})_2(\text{Imid})]_2$

The complex (reddish brown) was prepared by the procedure similar to that given for $[\text{Co}(\text{TP})_2\text{Py}]_2$ in (iii) except that pyridine was replaced by imidazole.

It has been observed that in the absence of a base the reactions given in (iii) to (vi) did not take place. Further, dibasic nitrogen bases like α,α -bipyridil or 1,10-phenanthroline did not yield any complex of cobalt(II) with TPH.

(vii) Bis(pyridine)tetrakis(N-carbamoylpyrrole-2-thiocarboxamidato)dicobalt(II), $[\text{Co}(\text{CPT})_2\text{Py}]_2$

An ethanolic solution of the ligand was treated with an equivalent amount of an aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ containing relatively an excess (10 ml) of pyridine at low temperature (5°C) with stirring. A yellow coloured complex formed was centrifuged out, washed several times with hot water,

small quantity of ethanol, diethyl ether and dried in vacuo. The complex was analysed as $[\text{Co}(\text{CPT})_2\text{B}]$.

(viii) Bis(β -picoline)tetrakis(N-carbamoylpyrrole-2-thiocarboxamidato)dicobalt(II), $[\text{Co}(\text{CPT})_2(\beta\text{-pic})]_2$

The yellow coloured complex was synthesized by a procedure similar to that described in (vii) except that β -picoline was used in place of pyridine.

(ix) Bis(γ -picoline)tetrakis(N-carbamoylpyrrole-2-thiocarboxamidato)dicobalt(II), $[\text{Co}(\text{CPT})_2(\gamma\text{-pic})]_2$

The yellow coloured complex was prepared by the same method as given in (vii) except that γ -picoline was used in place of pyridine.

(x) Bis(imidazole)tetrakis(N-carbamoylpyrrole-2-thiocarboxamidato)dicobalt(II), $[\text{Co}(\text{CPT})_2(\text{Imid})]_2$

The complex was prepared by the method similar to that described in (vii) except that pyridine was replaced by imidazole.

(xi) Reactions of TPH and CPTH with $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}(\text{en})_3]\text{Cl}_3$

An equivalent amount of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ or $[\text{Co}(\text{en})_3]\text{Cl}_3$ in aqueous solution was treated with an excess of ligand

(✓3 times) in ethanolic solution and the reaction was carried out in the manner as described for the preparation of $[\text{Co}(\text{TP})_2] \cdot 2\text{H}_2\text{O}$ in (ii). With CPTH and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, the product analysed was $[\text{Co}(\text{CPT})_2]$ while when $[\text{Co}(\text{en})_3]\text{Cl}_3$ was used as starting material, the products approximately analysed as $[\text{Co}(\text{en})(\text{TP})_{1/2} \text{S}_{3/2}] \cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{CPT})_2]$.

(xii) Reaction of anhydrous CoCl_2 ⁸ with TPH in argon atmosphere

A solution (25 ml) of CoCl_2 in abs. ethanol (degassed by passing argon gas) was treated with dried pyridine (5 ml) and to the resulting solution was added a solution (25 ml) of TPH (1:4 molar ratio) in abs. ethanol under argon atmosphere. The resulting mixture was refluxed for about 1 hour and the green solution thus obtained slowly evaporated to almost dryness keeping the inert atmosphere intact. The pasty mass was washed several times with dry ether till free from ligand and cobalt. To ensure the purity of the complex, it was recovered again by dissolving in abs. ethanol and evaporating and washing with dry ether. The product analysed for $[\text{Co}(\text{py})_4\text{Cl}_2]$ after drying it over P_4O_{10} . When the complex was treated with the ligand in water-ethanol and refluxed for 30 min, the product obtained was the same as obtained in reaction (iii).

(xiii) Reaction of anhydrous $[\text{CoCl}_2]$ with CPTH in argon atmosphere

This reaction was carried out by the same method as that given in (xii) except that CPTH was used in place of TPH. However, the product could not be purified owing to the insolubility of the ligand in ether.

Analyses

Sulphur content in the complexes was estimated as BaSO_4 by decomposing them according to the procedure as described in Chapter II. Cobalt was estimated by decomposing a known weight of the sample with aquaregia, precipitating with α -nitroso- β -naphthol and subsequent weighing as cobalt sulphate.⁹

C, H, N were analysed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India. Results are given in Table III.1.

Infrared and UV-visible spectra of the ligands and the complexes were recorded as described in Chapter II. Magnetic susceptibility measurements were made on a standard Gouy balance. The susceptibility tube was corrected using mercury(II) tetra-thiocyanato cobalt(II) as standard. The appropriate correction for the diamagnetic susceptibility was applied. The molar susceptibility values are corrected for the diamagnetism of the organic ligands (Table III.1).

RESULTS AND DISCUSSION

Although the ligands contain two (or three) nitrogens, one sulphur and one oxygen atoms capable of coordinating with the metal ion, simultaneous involvement of all these donor atoms in bond formation is a rare possibility. Based upon analytical results, it is concluded that the ligand is acting as bidentate chelating (or bridging) in all the complexes. Although IR spectra of the ligand¹⁰ and complexes are very complicated owing to the extensive overlap of a number of bands arising due to the various modes of vibrations of CO, NH, CS, C=C, and CN groups in the region below 1800 cm^{-1} , there are some bands which have been assigned with some degree of certainty because of the systematic shifts in their positions.

The spectra of the complexes showed the characteristic bands of pyrrole¹¹ ring ($3160, 1550, 1460, 1400, 1120, 1035, 995, 885, \text{ and } 750\text{ cm}^{-1}$) ($\pm 5\text{ cm}^{-1}$). This indicated the non-involvement of pyrrole ring nitrogen in the coordination. It is also quite in conformity with the facts: (1) The ring nitrogen in pyrrole is poorly basic and that the deprotonation of pyrrole NH group occurs only in the highly basic medium. It is, therefore, assumed that bonding in complexes takes place through -C(S)NHC(O)- moiety of the ligands and the major shifts in the positions of the bands corresponding to these groups should be in those of thioamide and amide ones.

Co(II) Complexes of TPH

In the complexes $[\text{Co}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{TP})_2\text{B}]$ and $[\text{Co}(\text{TP})_2]\cdot 2\text{H}_2\text{O}$, due to the extensive mixing between the bands of ligand and those of the bases, the characteristic five- or six-membered ring frequencies¹¹ of the heterocyclic bases did not occur at their standard position. The spectra of the complexes were analysed on the following grounds: (a) The band due to $\nu(\text{NH})$ which occurred around 3210 cm^{-1} in the spectra of the ligand was shifted to higher wave number side (60 cm^{-1}) in the spectra of the complexes suggesting deprotonation of the NH group of $-\text{C}(\text{S})\text{NHC}(\text{O})-$ moiety. (b) The band due to $\nu(\text{C}=\text{O})$ (1765 cm^{-1}) of the ligand was shifted to lower wave number (20 cm^{-1}). (c) The thioamide (IV)¹² band in the ligand shifted to higher wavenumber (10 cm^{-1}). (d) There were no systematic shifts in the positions of the thioamide $-\text{N}-\text{C}=\text{S}$ bands (II) and (III) and amide bands (II) and (III) in the region $1550-1200\text{ cm}^{-1}$ of the complexes as expected for the vibrational modes having contributions from $\nu(\text{CN})$, $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{S})$. (e) Two new bands of lower intensity in the spectra of the complexes around 460 and 560 cm^{-1} were assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$, respectively.¹³ These shifts could be explained if the bonding in these complexes was assumed through N and O atoms of the $-\text{C}(\text{S})\text{NHC}(\text{O})-$ moiety of the ligand and one of the axial positions was occupied by the base, thus supporting a square pyramidal geometry around the metal ion. A peak around

140°C was obtained in the DTA curve showing that water molecules are not coordinated.

The complex $\text{Co(Py)}_4\text{Cl}_2$ did not exhibit the characteristic $\nu(\text{C=O})$ frequency of the ligand, instead it displayed characteristic frequencies of pyridine. The magnetic moment to the extent of three unpaired electron (4.1 BM) indicated the octahedral geometry around the metal. ()

Co(II) Complexes of CPTH

In the IR spectra of these complexes, $\nu(\text{C=O})$ shifted to lower wavenumber ($\Delta\nu$ 25 cm^{-1}) suggesting the bond formation through oxygen of carbonyl group. Three bands around 3400, 3375 and 3250 cm^{-1} in the spectra of the ligand assigned to $\nu(\text{NH})$ were present in the spectra of the complexes except that the band at 3250 cm^{-1} was shifted to lower wavenumber side. The position of the thioamide-band IV shifted to higher wavenumbers or remained stationary in some complexes. Bands present between 1650 and 1300 cm^{-1} shifted to higher wavenumbers. The new bands around 525 and 450 cm^{-1} assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})^9$, respectively.

Magnetic Properties

All the complexes reported herein except the $[\text{Co}(\text{TP})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{Py})_4\text{Cl}_2]$, are unusually^{14,15} diamagnetic. It is significant to note that when starting material was Co(II), the

complexes formed were diamagnetic while with Co(III), paramagnetic complex was obtained. The magnetic moment value (1.65 B.M.) was less than that was generally observed in one unpaired electron case in square planar cobalt(II) compound.¹⁶ This suggested that cobalt(III) was reduced to cobalt(II) giving unpaired electron. Lowering in the μ_{eff} value may be due to (i) Co(II) and Co(III) mixed valence complex formation and (ii) partial dimerisation of the compound in solid state resulting into the partial spin pairing of the electron.

Attempts to oxidise the diamagnetic complexes of TPH and CPTH using a dilute solution of Br_2 in CCl_4 resulted in the partial decomposition of the complex to the Co(II) ions and the free ligand, which were identified via thiocyanate test and melting points of the ligands, respectively. The possibility of the metal ions being oxidized to +3 state in diamagnetic complexes has been ruled out on the following facts: (a) Since the ligand under the same experimental conditions reduces cobalt(III) to Co(II) giving rise to paramagnetic complex, it can not act as oxidizing agent under the same condition. (b) When the reaction is carried out under an inert and strictly anhydrous atmosphere (i.e. under argon atmosphere) oxidation of metal ion is not observed. (c) When oxygen or nitrogen gas was passed into DMF solution of the diamagnetic complexes, no change in colour was observed. (d) For the cobalt to be present in +3 oxidation state, one of the ligand molecules has to act as

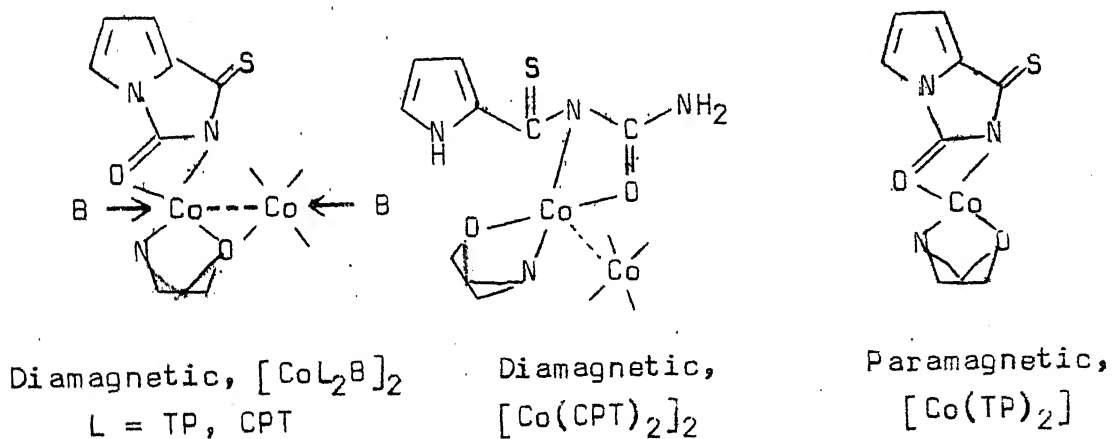
dianion which is quite unlikely under the experimental conditions. It is, therefore, assumed that the oxidation state of cobalt is +2 in all the diamagnetic complexes. Unlike the earlier reports³ the complexes $\text{Co}(\text{TP})_2\text{B}$ and $\text{Co}(\text{CPT})_2\text{B}$ are found to be diamagnetic and attempts to prepare a paramagnetic complex of this composition met with failure. However, previous reports of the square pyramidal complex in presence of pyridine is found to be correct. This prompted us to believe that these ligands act differently than the earlier ones³, may be due to the difference in the end groups (ring NH, $-\text{NH}_2$ as against $-\text{OEt}$ and $-\text{NHPh}$ in the earlier report).

Cobalt(II) being d^7 system, its complex should show paramagnetism either equivalent to three unpaired electrons (O_h or T_d symmetry) or equivalent to one unpaired electron (square planar geometry). The observed diamagnetism of the complex indicates spin pairing occurring via the formation of bond between two Co(II) ions with the ligand molecule in the square planar or square pyramidal geometry. The Co---Co interaction may take place either between two $\text{Co}(\text{TP})_2\text{B}$ (or $\text{Co}(\text{CPT})_2$, $\text{Co}(\text{CPT})_2\text{B}$) monomer units in the solid state or the complexes exist as ligand-bridged dimer, trimer or oligomer, like $\text{Co}(\text{acac})_2$ which would perhaps force some Co---Co interaction on the system making it diamagnetic. Due to low solubility of the complexes in benzene or bromoform it was not possible to find out its molecular weight which would have provided useful information

regarding the extent of polymerisation. The spin pairing may also take place by the formation of extended MOs by the extended overlap of metal and donor atoms orbital. It is also a known fact¹⁷ that donor atoms like As, P or S possess greater tendency to spin pairing. It is not possible to decide explicitly between these possible mechanisms of spin pairing on the magnetic data alone.

If the facts gathered so far are to be compatible, the following geometry (Chart 1) can be assigned to the complexes:

CHART 1



Electronic Spectra

The chloroform solution of TPH and CPTH exhibited bands at 27000, 30303, 35088, 36363 cm^{-1} and 28570, 34483 cm^{-1} , respectively. The lower energy side bands may be due to the transition involving N and S¹⁸ (less intense than $\pi \rightarrow \pi^*$

transition). The other two bands may be assigned to the intra-ligand charge transfer bands.

Owing to the low solubility of the complexes in CHCl_3 , the electronic spectra were recorded in DMF. The diamagnetic complexes of TPH and CPTH exhibited bands in the lower energy region at $8333(\text{w}, \text{br}) \text{ cm}^{-1}$, 7000 cm^{-1} and $6000(\text{w})$, $5220(\text{s}) \text{ cm}^{-1}$, respectively. The high energy side bands occurred in the diamagnetic complexes of both the ligands around 24400 , 26770 , 35700 , 24700 and 35460 cm^{-1} , respectively. The lower energy side bands in the near IR region may be due to the overtones or combination bands of $\nu(\text{C-H})$ or (N-H) . The band around 8333 cm^{-1} in $[\text{Co}(\text{TP})_2\text{B}]_2$ may be assigned to ν_1 . The paramagnetic complex $\text{Co}(\text{TP})_2 \cdot 2\text{H}_2\text{O}$ exhibited band at $25000(\text{w})$, $27000(\text{w})$ and $36000(\text{s}) \text{ cm}^{-1}$. The third one may be due to charge transfer transitions.¹⁹ The near IR spectrum showed ~~a~~ very broad bands around 8333 , 6666 and 6000 cm^{-1} .

It is not quite conclusive as to which geometry can be assigned to the complexes on the basis of these transitions. Most of the d-d transitions were masked by strong CT and intraligand transitions.

No signal in EPR spectrum of the paramagnetic complex appeared either at room temperature or at 77 K . The compound was taken in quartz tube along with DPPH ($g = 2.0036$). The non-occurrence of the signal may be due to reduced spin-

relaxation time to greater extent because of the very low separation between the ground state and the next higher state.

Thus, on the basis of elemental analyses, infrared, electronic spectral studies and magnetic measurement data, the tentative geometry assigned to the complexes are given in Table III.1.

Table III.1

Magnetic and Analytical Data of the Complexes

Complexes	μ_{eff} (B.M.)	Colour	Found (Calcd) %							Suggested Geometry
			C	H	N	S	Cl	M		
1	2	3	4	5	6	7	8	9	10	
$[\text{Co}(\text{TP})_2\text{Py}\cdot 2\text{H}_2\text{O}]_2$	D	BB	42.3 (42.9)	3.4 (3.2)	16.7 (16.8)	13.7 (13.5)	-	12.4 (12.2)	spy	
$[\text{Co}(\text{TP})_2\cdot \text{Imid}]_2$	D	RB	42.4 (42.1)	2.2 (2.3)	19.5 (19.6)	15.2 (15.0)	-	13.3 (13.6)	spy	
$[\text{Co}(\text{TP})_2\cdot \beta(\gamma)\text{pic}]_2$	D	RB	47.5 (47.7)	2.8 (2.9)	15.3 (15.5)	13.9 (14.1)	-	13.0 (12.8)	spy	
$[\text{Co}(\text{TP})_2\cdot 2\text{H}_2\text{O}]$	1.65	BB	36.6 (36.3)	2.4 (2.5)	14.2 (14.2)	16.4 (16.2)	-	14.8 (14.6)	sq.pl.	
$[\text{Co}(\text{CPT})_2]_2$	D	R	36.1 (36.3)	3.4 (3.3)	20.9 (21.3)	16.4 (16.2)	-	14.4 (14.6)	sq.pl.	
$[\text{Co}(\text{CPT})_2\text{Py}]_2$	D	Y	42.9 (43.1)	2.2 (2.3)	19.9 (20.7)	13.8 (13.6)	-	12.5 (12.3)	spy	
$[\text{Co}(\text{CPT})_2\cdot \text{Imid}]_2$	D	Y	39.3 (39.0)	3.3 (3.5)	24.1 (24.2)	13.7 (13.8)	-	12.3 (12.6)	spy	

Table III.1 (contd.)

1	2	3	4	5	6	7	8	9	10
[Co(CPT) ₂ .β(γ)pio] ₂	D	Y	44.1 (44.4)	4.1 (3.9)	19.8 (20.1)	13.3 (13.1)	-	12.1 (11.9)	spy
[Co(PY) ₄ Cl ₂]	4.1	G	54.3 (53.9)	4.2 (4.5)	12.5 (12.6)	-	16.2 (16.0)	12.7 (13.0)	Oh

D, diamagnetic; BB, black brown; RB, red brown; R, red; Y, yellow; G, green;
 Py, pyridine; Imid, imidazole; pic, picoline; spy, square pyramidal; sq.pl., square
 planar; Oh, octahedral.

LEGEND TO THE FIGURES

Fig. III.1 Infrared Spectra

1. $[\text{Co}(\text{TP})_2\text{Py}]_2 \cdot 4\text{H}_2\text{O}$
2. $[\text{Co}(\text{TP})_2 \cdot \text{Imid}]_2$
3. $[\text{Co}(\text{TP})_2] \cdot 2\text{H}_2\text{O}$
4. $[\text{Co}(\text{Py})_4\text{Cl}_2]$
5. $[\text{Co}(\text{CPT})_2]_2$
6. $[\text{Co}(\text{CPT})_2 \cdot \text{Imid}]_2$

Fig. III.2 Near IR, UV-Visible Spectra

- A. $[\text{Co}(\text{TP})_2] \cdot 2\text{H}_2\text{O}$
- B. $[\text{Co}(\text{CPT})_2]_2$
- C. $[\text{Co}(\text{TP})_2\text{Py}]_2 \cdot 4\text{H}_2\text{O}$
- D. $[\text{Co}(\text{CPT})_2]_2$

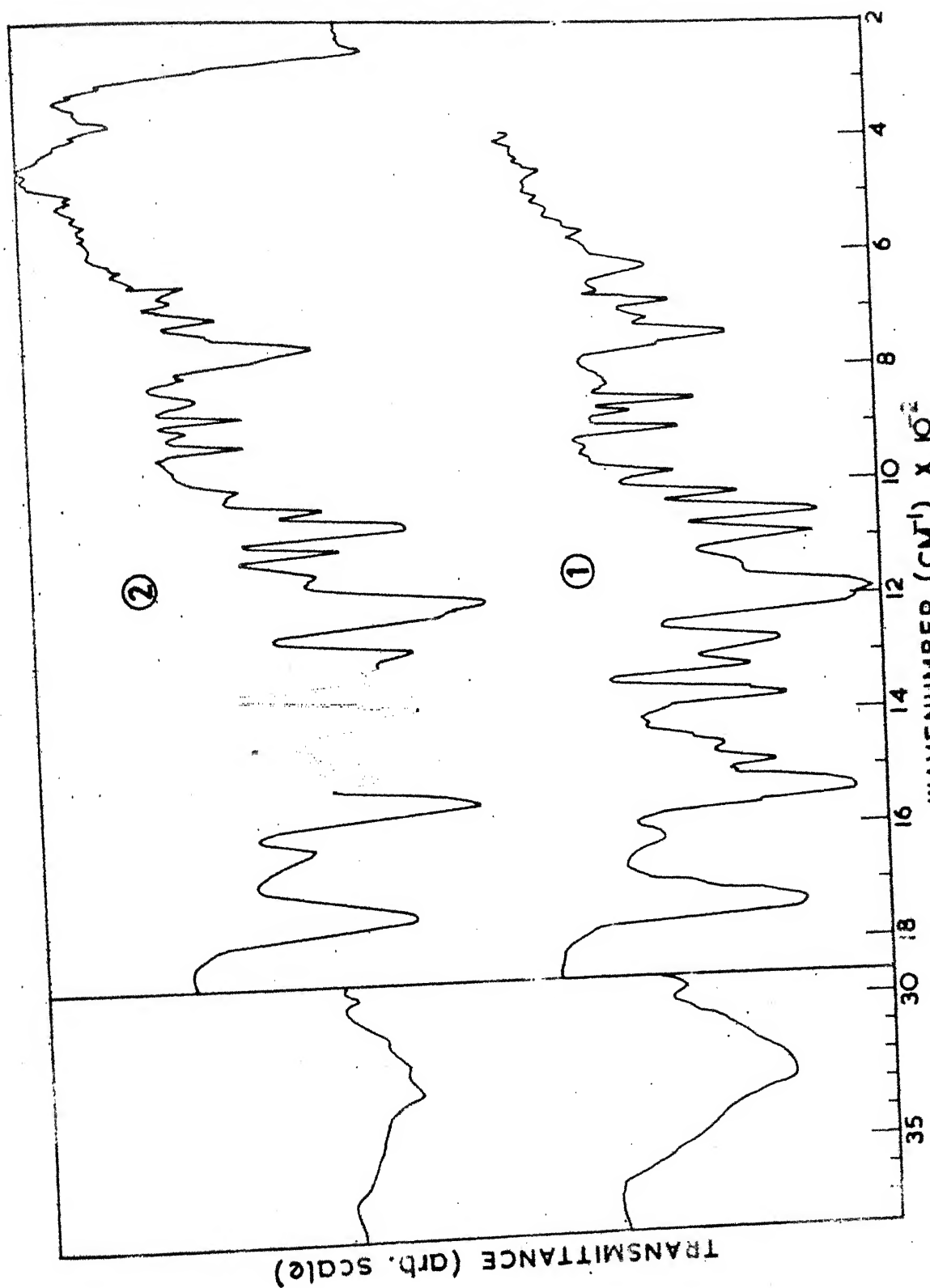


FIG. III.1

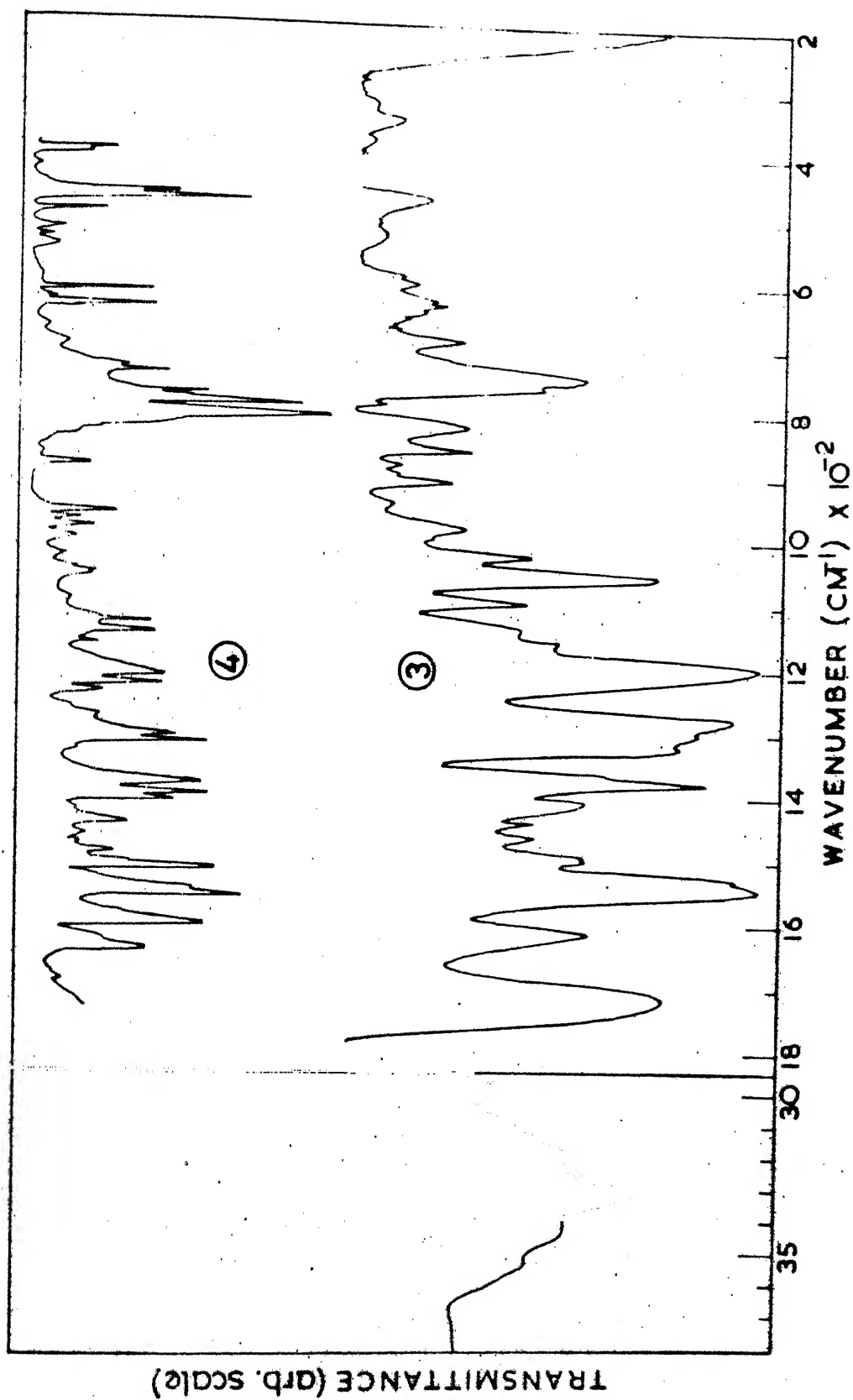


FIG. III.1

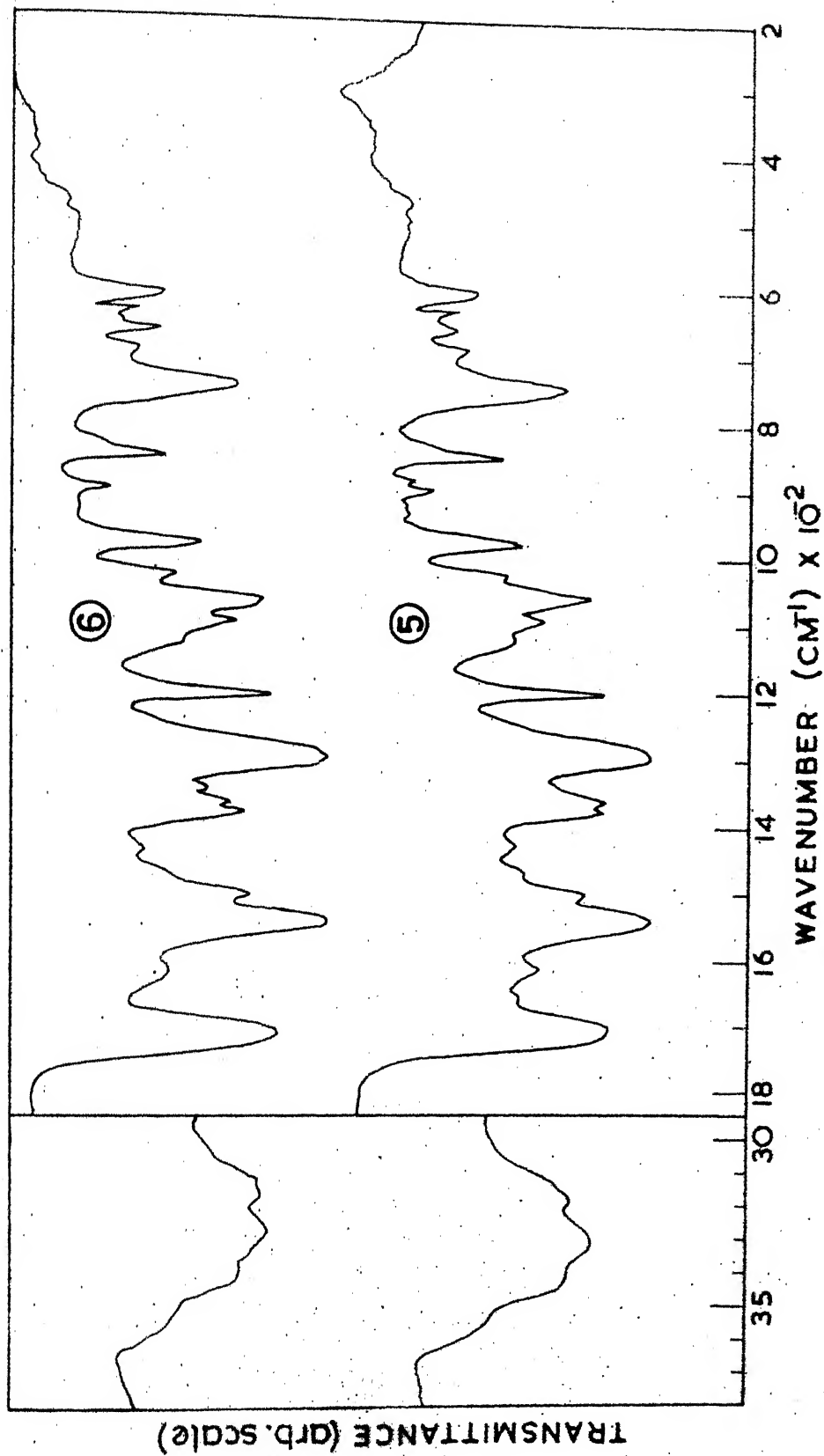


FIG. III.1

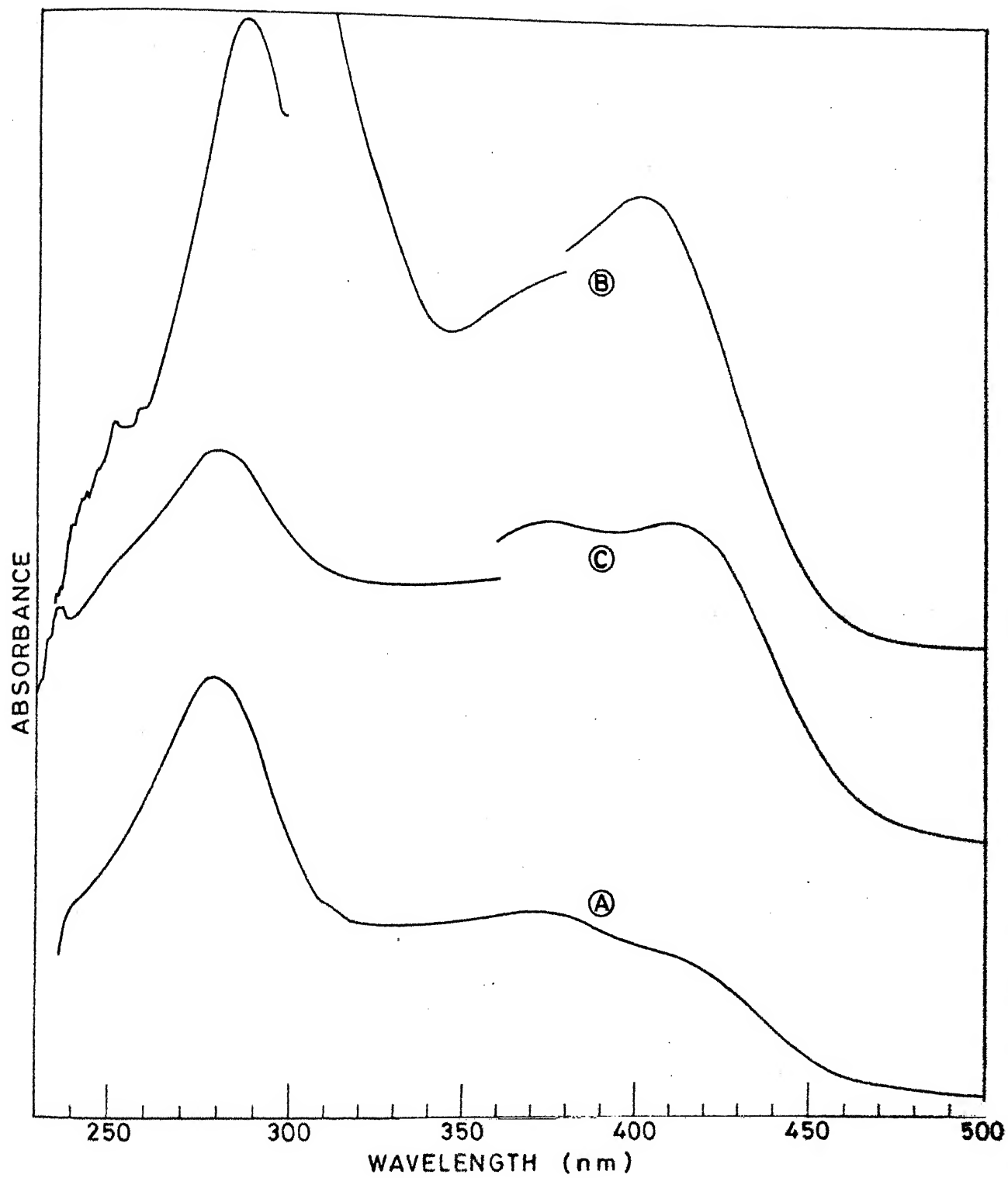


FIG. III. 2

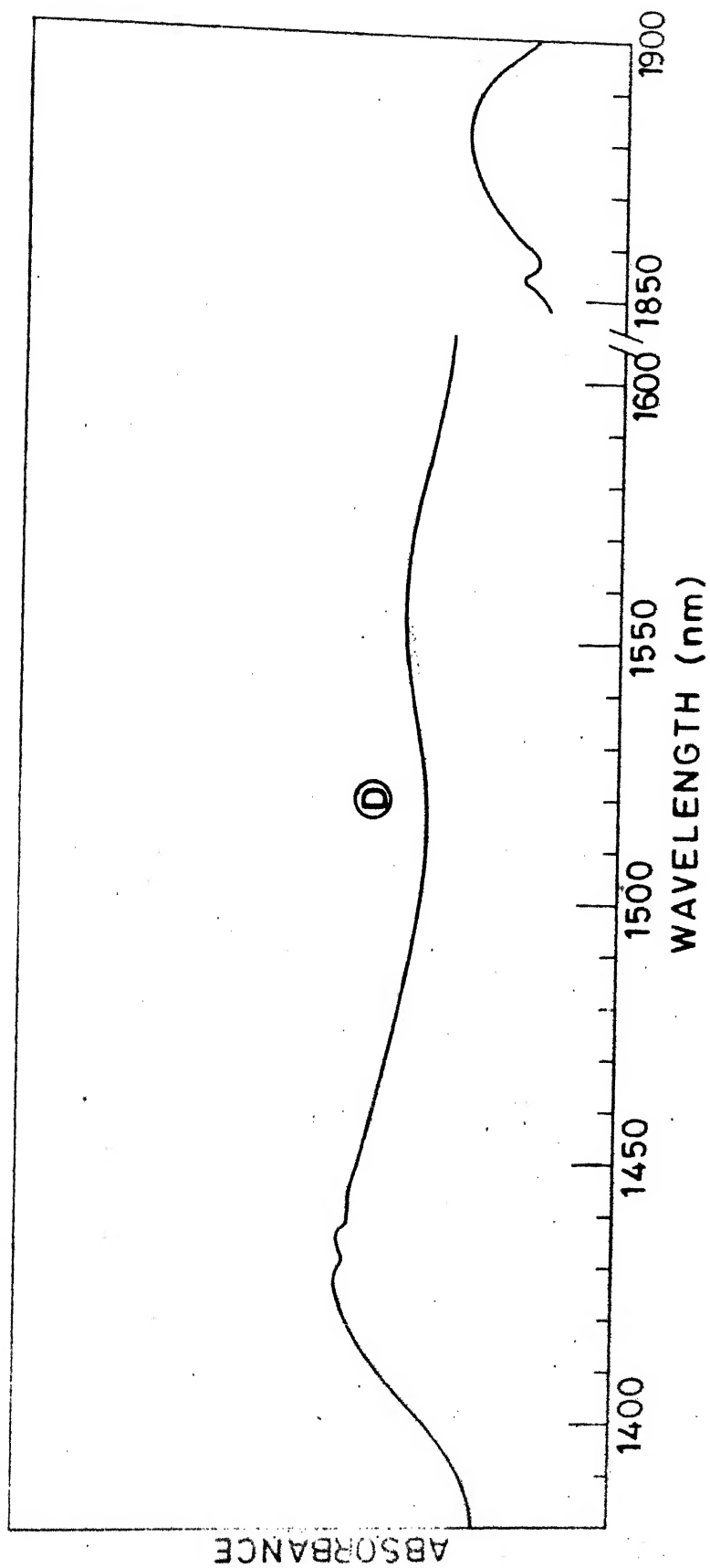


FIG. III.2

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CHAPTER IV

REACTIONS OF NICKEL(II) AND COPPER(II) IONS WITH 2-THIOPYRROLE-1,2-DICARBOXIMIDE AND N-CARBAMOYLPYRROLE-2-THIOCARBOXAMIDE IN PRESENCE OF VARIOUS NITROGEN CONTAINING HETEROCYCLIC BASES

This chapter describes the syntheses, the physical and chemical properties of nickel(II) and copper(I) complexes with 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH). Their tentative structures have been proposed on the basis of the analytical, magnetic and spectral (UV-Visible and IR) studies.

EXPERIMENTAL

All the chemicals used were either chemically pure or AnalaR grade. Ligands, TPH and CPTH, were prepared by the methods as described in Chapter II.

Preparation of the Metal Complexes

(i) Monopyridinebis(2-thiopyrrole-1,2-dicarboximidato)-nickel(II) dihydrate, $[\text{Ni}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$

25 ml of an ethanolic solution of the ligand (0.5 g, 3 mmol) was slowly added with stirring to an aqueous solution (30 ml) of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ (0.4 g, 1.5 mmol) containing about 1 ml of pyridine, whereby an intense reddish violet solution was obtained. It was refluxed for about half an hour on a water bath. This resulted in the formation of reddish coloured crystalline product which was separated by centrifugation, washed successively with water, small amounts of ethanol, diethyl ether and dried in vacuo. In the centrifugate, excess water was further added and refluxed on a water bath to precipitate more of the complex. The complex did not melt upto 200°C . It was observed that the complex did not precipitate in the absence of base.

(ii) Mono(β -picoline)bis(2-thiopyrrole-1,2-dicarboximidato)-nickel(II) monohydrate, $[\text{Ni}(\text{TP})_2(\beta\text{-pic})]\cdot \text{H}_2\text{O}$

The complex was prepared by the same method as described in (i) except that β -picoline was used in place of pyridine.

(iii) Mono(γ -picoline)bis(2-thiopyrrole-1,2-dicarboximidato)-nickel(II) monohydrate, $[\text{Ni}(\text{TP})_2(\gamma\text{-pic})]\cdot\text{H}_2\text{O}$

The complex was synthesized by the same procedure as described in (i) except that γ -picoline was used in place of pyridine.

(iv) Mono(imidazole)bis(2-thiopyrrole-1,2-dicarboximidato)-nickel(II) dihydrate, $[\text{Ni}(\text{TP})_2\text{Imid}]\cdot 2\text{H}_2\text{O}$

The method of preparation of this compound was same as that described in (i) except that imidazole was used in place of pyridine.

(v) Monopyridine(2-thiopyrrole-1,2-dicarboximidato)(2-thiopyrrole-1,2-dicarboximide)copper(I) monohydrate, $[\text{Cu}(\text{TP})(\text{TPH})\text{Py}]\cdot\text{H}_2\text{O}$

25 ml of an aqueous solution of copper sulphate pentahydrate (0.25 g, 1 mmol) containing about 2 ml of pyridine was treated with an ethanolic solution (25 ml) of the ligand (0.35 g, 2.3 mmol). The colour of the solution was changed immediately to red followed by slow precipitation of the complex. The mixture was stirred for five minutes and allowed to stand for about half an hour at room temperature. The product was separated by filtration, washed several times with water, small amounts of ethanol and finally with diethyl ether. It was dried under vacuo.

In case the metal salt solution was treated by the method described above with the ligand solution in the absence of pyridine, a compound that formed was best analysed for $[\text{Cu}_2(\text{TP})_2(\text{TPH})\cdot\text{H}_2\text{O}]$. It did not melt upto 280°C .

(vi) Monoimidazole(2-thiopyrrole-1,2-dicarboximidato)(2-thiopyrrole-1,2-dicarboximide) copper(I) monohydrate,
 $[\text{Cu}(\text{TP})(\text{TPH})\text{Imid}]\cdot\text{H}_2\text{O}$

This compound was prepared by the method similar to one described in (v) except that imidazole was used in place of pyridine.

(vii) Bis(N-carbamoylpyrrole-2-thiocarboxamidato)nickel(II),
 $[\text{Ni}(\text{CPT})_2]$

25 ml of an ethanolic solution of the ligand (CPTH) was treated with an aqueous solution of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ in 1:2 molar ratio. The resulting solution was refluxed for about half an hour, whereby a red crystalline precipitate settled down which was suction filtered, washed successively with water, ethanol, diethyl ether and dried in vacuo.

(viii) N-Carbamoylpyrrole-2-thiocarboxamidato)(N-carbamoylpyrrole-2-thiocarboxamide) copper(I) monohydrate,
 $[\text{Cu}(\text{CPT})(\text{CPTH})]\cdot\text{H}_2\text{O}$

This compound was prepared by the method similar to the one described in (v) except that CPTH was used in place of

TPH and 0.1 ml of pyridine was used.

ANALYSES

Estimation of metal

A weighed amount of complex was decomposed by digesting it with aquaregia for sometime until the resulting residue gave a transparent solution when taken in the mineral acids. Excess of HNO_3 from the residue was removed by the repeated evaporation with HCl and then with water until the solution became almost neutral (pH paper). Nickel¹ was estimated in this solution by precipitating it with dimethylglyoxime and weighing as $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$. Copper was estimated from the above solution as $[\text{Cu}(\text{en})_2][\text{HgI}_4]$.

Estimation of sulphur, carbon, hydrogen and nitrogen

These were done exactly in the manner described in Chapter II. Analytical results for these complexes are presented in Table IV.1. Since the recrystallisation of the complexes was not possible owing to the lack of their solubility in suitable solvents, they were repeatedly analysed to give the consistent analytical results.

Infrared Spectra

Infrared spectra of the complexes and the ligands were recorded with a Perkin-Elmer 580 Diffraction Grating Infrared

Spectrophotometer in the range $4000-200\text{ cm}^{-1}$. Samples were prepared as potassium bromide pellets. The positions of the major infrared bands of the ligands and the complexes have been found to be similar to those presented in Table II.2 (Chapter II).

Magnetic Susceptibility Measurements

Magnetic susceptibility of the complexes were determined with the help of a standard Gouy balance at room temperature. All the complexes described in this chapter are diamagnetic.

Near IR, UV and Visible Spectra

The absorption spectra of the ligands and the complexes were measured in chloroform (or in nujol) on a Cary-17D model spectrophotometer in the range $1800-200\text{ nm}$. The data are tabulated in the Table IV.3 and the results are described in the text.

RESULTS AND DISCUSSION

The analytical results of the complexes of nickel and copper with TPH and CPTH correspond to the formulae indicated in Table IV.1. TPH complexes of nickel were found to be slightly soluble in ethyl alcohol and acetone and soluble in chloroform, dichloromethane, nitrobenzene, DMF, DMSO and other

similar organic solvents. Copper complexes of TPH and CPTH and the nickel complex of CPTH were slightly soluble in these solvents. All the complexes are high melting, diamagnetic solids.

Since ligands are polyfunctional and possess four potential donor atoms, infrared spectra of the ligands² and those of the complexes were compared in order to decide the bonding sites. Owing to the extensive mixing of $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{S})$, $\nu(\text{NH})$ modes, the infrared spectra were highly complicated to decide explicitly the assignments of the various bands by the presence of a number of IR bands. The complication was further enhanced by the bases linked to the metal ion in the spectra of the complexes. Obviously, unambiguous assignment of the bands and locating the donor sites was not possible. However, on comparing all the spectra of the complexes with that of the ligand a few points emerged which were common in all of them. There were systematic shifts in the positions of a few bands which gave certain clues to explore the bonding sites in the ligands. Also, the characteristic frequencies of the pyrrolo ring were mixed with those of the other heterocyclic bases.³ On the basis of the arguments described in Chapter II and Chapter III, the noninvolvement of pyrrole ring nitrogen in the bond formation with the central metals is also retained here. It is, therefore, assumed that the bonding may be taking place through $-\text{NC}(\text{S})-\text{NH}-\text{C}(\text{O})-$ moiety of the ligands.

Thus, the assignments of a few bands along with the possible bonding are discussed. For the sake of clarity of the discussion, the complexes of similar type are grouped together.

Ni(II) Complexes of TPH

The spectra of the complexes, $[\text{Ni}(\text{TP})_2 \cdot \text{B}] \cdot x\text{H}_2\text{O}$, were almost similar. The systematic shifts were more or less in the same direction but the wavenumbers by which the positions of the bands shifted were slightly different (Table IV.2). The major changes in the band positions in spectra of the complexes to those of the ligand are as follows:

(i) The position of the band due to $\nu(\text{NH})$ at around 3200 cm^{-1} disappeared in the complexes and new bands appeared around 3300 cm^{-1} which may be characteristic bands of the respective bases present in the complexes. This suggested the deprotonation of the imide ring of the ligand which was also indicated by the charge balance in the complexes.

(ii) The position of the amide band I, having major contribution from $\nu(\text{CO})$, which appeared at around 1765 cm^{-1} in the spectrum of the ligand shifted (sometime with splitting) towards lower wavenumbers in the spectra of the complexes, which indicates the involvement of the carbonyl oxygen in the bond formation⁴ with the central metal atom.

(iii) The bands 1560 and 1440 cm^{-1} present in the

spectrum of the ligand shifted to lower wave number region whereas that at 1350 cm^{-1} disappeared in the spectra of the complexes. The positions of the ligand bands due to the amide III and thioamide II and III in the region $1350\text{--}1190\text{ cm}^{-1}$ remained almost stationary in the spectra of the complexes. These bands have been assigned to the mixed vibrations having contributions from $\nu(\text{C}=\text{N})$, $\delta(\text{NH})$, $\delta(\text{C}=\text{C})$, $\delta(\text{CH})$ modes. The shifting of the band position of 1560 cm^{-1} and 1440 cm^{-1} suggests the bonding through nitrogen after deprotonation which was also corroborated by the absence of the band at 3200 cm^{-1} due to $\nu(\text{NH})$.

(iv) The 966 cm^{-1} band present in the spectrum of the ligand was absent in the spectrum of picoline complex but was present in the spectra of the other two complexes with a small negative shift.

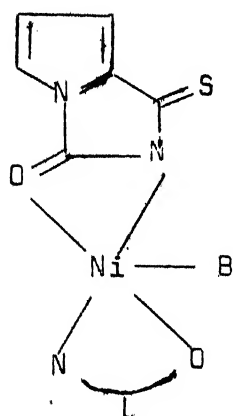
(v) The thioamide band IV⁵ (around 840 cm^{-1}) which has major contribution from $\nu(\text{C}=\text{S})$, was either split into two or remained stationary in the spectra of the complexes. It suggested that the thiocarbonyl sulphur is not the bonding site.

(vi) New bands of medium intensity in the region $500\text{--}300\text{ cm}^{-1}$ appeared in the spectra of the complexes. These bands were assigned to $\nu(\text{M}-\text{O})$ or $\nu(\text{M}-\text{N})$ modes of vibration.

(vii) The additional bands, marked with star in

Table IV.2, observed in the IR spectra of the complexes may be the characteristic bands of the heterocyclic bases.

In view of the above and if the preferred geometries around the metal ions are assumed, the following bonding sites in the metal complexes for the metal ions may be proposed (Structure I);



B indicates the base used

STRUCTURE I

Copper Complexes of TPH and CPTH

Copper complexes of TPH and CPTH were analysed for $[\text{Cu}(\text{TP})(\text{TPH})\text{B}]\cdot\text{H}_2\text{O}$ (B = pyridine, imidazole) and $\text{Cu}(\text{CPT})(\text{CPTH})$, respectively. The systematic shifts in the band positions along with the assignments of the major bands are as follows:

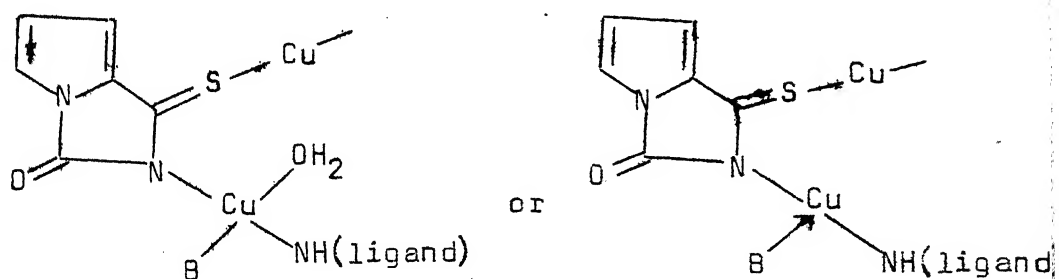
(i) The 3200 cm^{-1} band due to $\nu(\text{NH})$ present in the spectrum of the ligand disappeared in the spectra of the complex and weak bands around 3440 and 3360 cm^{-1} appeared. The band at 3100 cm^{-1} of the NH group of pyrrole remained stable. In the spectra of the CPTH complex all the ligand bands in the region $3500\text{-}2900\text{ cm}^{-1}$ disappeared except the ones

at 3380 cm^{-1} and 3270 cm^{-1} assigned to NH_2 group.

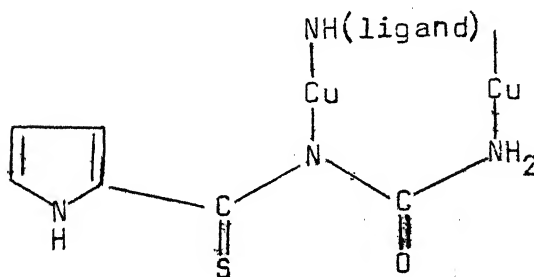
(ii) The position of the amide band I (ν_{CO}) was shifted towards higher wavenumber region in the spectra of the TPH complexes. The position of the same band in the spectra of CPTH complex practically did not, however, shift. This ruled out the possibility of bonding of metal ions through carbonyl oxygen and suggested that the nitrogen atom of the $-\text{C}(\text{O})\text{NHC}(\text{S})-$ moiety might be involved in the bond formation.

The diamagnetism of the complexes indicated copper ion to be in +1 oxidation state which shows that the ligand acted as reducing agent towards metal ion. Since two ligands are participating in the bond formation, one of the ligand molecules should act as neutral while the other as monobasic. There existed, however, another possibility where diamagnetism of the copper(II) complexes might arise because of the strong antiferromagnetic interactions between two cupric ions via the bridging S atom.⁶⁻⁸ It is undoubtedly very difficult to decide between the two alternatives. Since the ligands can act as reducing agent, the first alternative is relatively more preferred as compared to that of second. In case it is presumed that copper is present in +1 oxidation state, a linear geometry of the complex is preferred with bonding of the metal ion through nitrogen atom. The possibility of the copper complex having copper in +2 oxidation state may also be ruled out on

the basis of electronic spectra (*vide infra*) which did not show the characteristic band because of metal-metal interaction around 375 nm as observed by Yamada et al.^{6,7} in the spectra of the complexes where partial or complete quenching of magnetic moment occurred. Since these complexes have been found to be almost insoluble in the organic solvents, a polymeric structure (structures II and III) is proposed. However, the degree of polymerisation can not be decided by the spectral data. On the basis of the foregoing discussion the following tentative structure may be assigned to these complexes:



STRUCTURE II



STRUCTURE III

Nickel Complex of CPTH

(i) The band at 3200 cm^{-1} due to $\nu(\text{NH})$ of $-\text{C}(\text{O})-\text{NH}-\text{C}(\text{S})-$ moiety disappeared while the position of the other bands in this region remained practically the same.

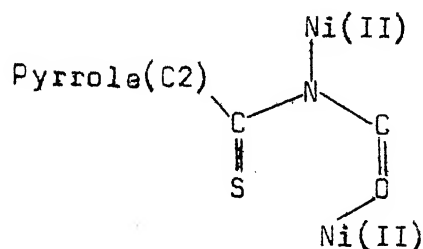
(ii) The position of the amide band (I), having major contribution from $\nu(\text{CO})$ shifted slightly to lower wavenumber (-5 cm^{-1}). The shift is so small that one may not feel confident of assigning carbonyl oxygen as bonding site. But the bonding of the metal ion with the nitrogen of $-\text{C}(\text{O})-\text{NH}-\text{C}(\text{S})-$ moiety will make the position of $\nu(\text{CO})$ to shift towards higher wavenumber. This will result in two opposing interactions, one trying to lower the $\nu(\text{CO})$ while the other to shift the position of $\nu(\text{CO})$ towards higher wavenumbers and thus causing a very small shift in the position of $\nu(\text{CO})$.

(iii) The shifts in the positions of thioamide bands and amide bands in the region 1500 cm^{-1} to 1200 cm^{-1} , on complexation were found to be varying. The positions of some of the bands shifted to higher wavenumber while those of the remaining ones to lower wavenumbers. It was, therefore, not possible to infer any thing out of these shifts.

(iv) The position of thioamide band (IV) having major contribution from $\nu(\text{C}=\text{S})$ shifted to higher wavenumbers ($+10\text{ cm}^{-1}$) corroborating the bonding of the metal ion through nitrogen of the $-\text{C}(\text{O})\text{NH}-\text{C}(\text{S})-$ moiety.

(v) The new bands also appeared in the region $300-400\text{ cm}^{-1}$. These may arise due to mixed vibrations of $\nu(\text{M-O})$ and $\nu(\text{M-N})$.

On the basis of the IR data, the following bonding scheme is tentatively proposed for the nickel complex;

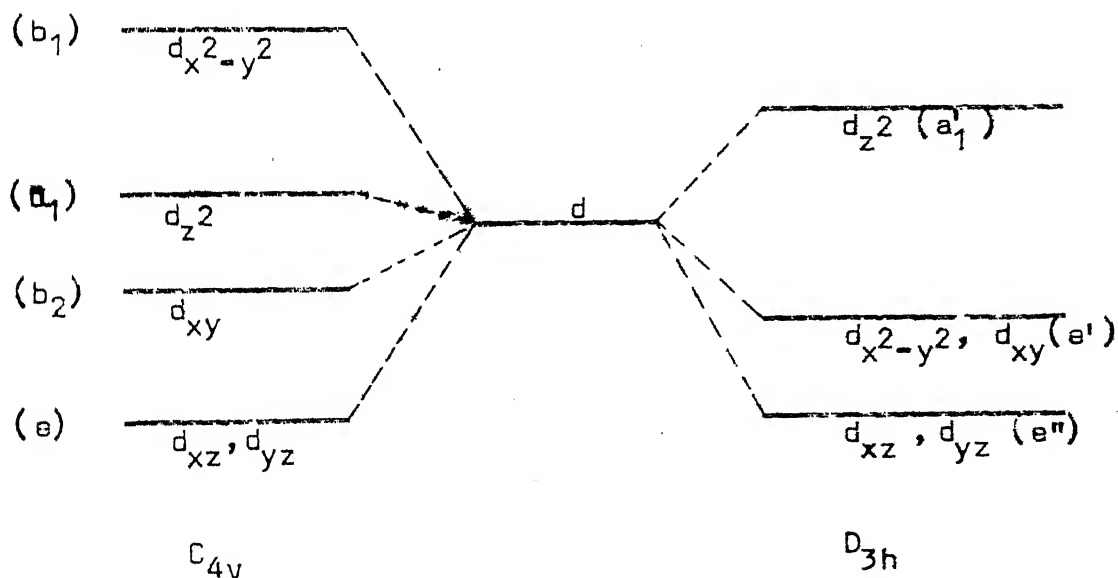


STRUCTURE IV

Magnetic Properties of Nickel and Copper Complexes

Nickel(II) being d^8 system, its diamagnetism is quite common with respect to square planar geometry. Since the complexes of nickel(II) with TPH were analysed for the coordination number five around the metal ion, both square pyramidal or trigonal bipyramidal geometries can be assigned to the complexes. Although the complexes having coordination number five are extensively studied and have been subject matter for several review articles⁹⁻¹⁷ dealing almost all aspects of chemistry, yet a clear picture of their nature regarding electronic spectra and stereochemical aspects is not explicitly explored. Five coordination complexes with d^5 , d^6 , d^7 or d^8 may be either high spin or low spin. Low spin complexes should

have one of the five d orbitals not available for occupancy.^{18,19} This non-availability of the fifth d orbital may be rationalised in terms of inner orbital dsp^3 hybridization. For trigonal-bipyramidal geometry, the d orbital involved in hybridization is d_{z^2} whereas in square pyramidal, it is $d_{x^2-y^2}$. Splitting of d orbitals in both fields (C_{4v} and D_{3h}) is presented in the following diagram for the sake of clarity of the explanation of the magnetic properties as well as the electronic spectra (vide infra) of these complexes:



In the present system, a π -delocalised system (refer to the structure of the ligand and bases) is dealt with and according to Orioli,¹⁴ it should favour square pyramidal geometry for five coordination since the possibility of π -bond formation in a square pyramid is more effective than that in trigonal bipyramidal

Because in the square pyramidal geometry, the d_{xy} , d_{yz} and d_{xz} metal d orbitals have full π -function whereas in trigonal bipyramid, it is only the d_{xz} and d_{yz} orbitals which have full π -function and d_{xy} and $d_{x^2-y^2}$ become partially σ -antibonding. Furthermore, coplanarity (which the ligand provides by acting as bidentate chelating) of the metal ion with the basal ligands make π -bonding more effective, specially with chelating ligands having a system of organic π -orbitals. Another important factor which favours square pyramidal geometry over trigonal bipyramidal one is the CFSE^{20,21} (and hence the oxidation state of the metal ion). For d^1 to d^9 electronic configuration (leaving out d^0 , d^5 , d^{10}) the CFSE is always higher for SP as compared to TBP geometry. Low spin complexes are generally formed with low electronegative donor atoms like S, P and As which are often involved in π -bond formation.²²

In spite of a long discussion in favour of square pyramidal geometry, which one of the two would be favoured depends markedly upon the fine balance of forces provided by the CFSE and nature of the metal to ligand bond (covalent vs ionic bonds; π -bonding) and various inter- and intraligand steric strains and repulsions. Indeed, the energy differences between the two geometries are so small that on some occasion the geometry is determined by the crystal packing forces which act through the formation of dimers, hydrogen bonding and influence of counter ions of particular shape. Since the

energy differences between the two geometries are small, distortion is unavoidable to the regular geometry of the complexes with five coordination and with large distortion, the multiplicity of the lowest energy state becomes singlet yielding a diamagnetic complex.²³ In view of the above, it is not possible to decide between a square pyramidal and trigonal bipyramidal geometry. However, square pyramidal geometry is tentatively assigned to the nickel complexes of TPH although trigonal bipyramidal geometry is not ruled out.

The nickel complex of CPT, $\text{Ni}(\text{CPT})_2$, has been found to be diamagnetic and hence a square planar geometry is assigned to it.

The diamagnetic behaviour of the copper complexes is interesting. The charge balance of the complex showed copper to be present in +1 oxidation state. Thus, the charge balance along with the magnetic data suggested that ligands have reduced copper(II) to copper(I). It seems all the more possible because sulphur ligands have a tendency to reduce copper from +2 to +1 oxidation state. However, another possibility exists for quenching the magnetic moment by metal-metal interaction²⁴ through the formation of a σ , π or δ -bond but the first alternative (reduction of Cu^{2+} to Cu^+) is preferred over the second.

Near IR, Visible and Ultraviolet Spectra

The complexes of nickel, viz. $[\text{Ni}(\text{TP})_2\text{Py}]$, $[\text{Ni}(\text{TP})_2\text{pic}]$, $[\text{Ni}(\text{TP})_2\text{Imid}]$ showed almost identical spectra recorded in chloroform as solvent in the region 1800-220 nm. The band positions and their assignments are listed in Table IV.3. These assignments are based on the assumption of square pyramidal geometry of the complexes. The lowest energy band was assigned to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. It is known²⁵ for a series of octahedral nickel complexes of the type $[\text{Ni}(\text{DMF})_6](\text{ClO}_4)_2$ and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_3$,²⁶ the lowest energy transition occurs at 8380 cm^{-1} (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$) and 10526 cm^{-1} (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$), respectively. Since there is a lowering of symmetry from O_h to C_{4v} point group one expects a drop in the value of ν_1 (ca. 7092 cm^{-1}) as well as increase in the number of bands in the electronic spectra which are well in agreement with the observed facts. The other lower energy bands are probably the ligand field bands which might be safely assigned to $xy \rightarrow x^2-y^2$ (1111 cm^{-1}). The other band occurred at 18180 cm^{-1} . The band around 8333 cm^{-1} did not appear in picoline and imidazole complexes. The other high energy transitions may be assigned to the charge transfer occurring due to highest occupied molecular orbital of the ligand to the lowest unoccupied metal orbitals, or intraligand charge transfer bands.

Owing to the very low solubility of $\text{Ni}(\text{CPT})_2$ in CHCl_3 , the spectrum was recorded in nujol. The intensity of the two

bands at 17857 cm^{-1} (broad) and 21277 cm^{-1} suggested them to occur due to d-d transition. The spectral bands for the similar dithio β -diketone complexes of Ni, Pd and Pt of general formula, $M(\text{OEt-SacSac})_2$, have been described by Martin et al.²⁷ The four uppermost occupied molecular orbitals and the lowest unoccupied were found to be predominantly metal in character²⁸ and the electronic ground d state configuration proposed for d⁸ complexes is $[d_{xy}]^2 [d_z^2]^2 [d_{xz}]^2 [d_{x^2-y^2}] [d_{xy}]^0$, in order of increasing energy. The band around 14700 cm^{-1} was assigned to $x^2-y^2 \rightarrow xy$ (d-d) transition whereas transition at 17500 cm^{-1} was assigned to $xz \rightarrow xy$ transition in $\text{Ni}(\text{OEt-SacSac})_2$ complex. However, the latter band was not commonly observed in other cases. Thus, taking the analogy under consideration, the band at 17857 cm^{-1} in the complex, $\text{Ni}(\text{CPT})_2$, could be assigned to $x^2-y^2 \rightarrow xy$ (${}^1A_{1g} \rightarrow {}^1B_{1g}$). The other band at 21277 cm^{-1} may be assigned to the $xz \rightarrow xy$ (${}^1A_{1g} \rightarrow {}^1B_{3g}$) transition which is at quite high energy as compared to dithio β -di-ketone complex.²⁹ These assignments are in agreement with the statement that the transition in complexes having the donor atoms which form σ type bond character (i.e., N and O) occur in high energy region.³⁰⁻³² The other two bands ($26320, 35714\text{ cm}^{-1}$) were assigned to the charge transfer, $[L(\pi) \rightarrow xy]$ and intraligand, $[L(\pi) \rightarrow L(\pi^*)]$ transition bands, respectively which involved thiocarbonyl group of the ligand.³³

The copper complex of TPH showed in its spectra (recorded in nujol) only two high energy broad bands with the maxima at 35714 cm^{-1} and 41667 cm^{-1} . These bands have been assigned to the intraligand charge transfer $[L(\pi) \rightarrow L(\pi^*)]$, transitions. Other copper complexes showed similar behaviour. On the basis of the above arguments the following tentative geometries have been assigned to the complexes:

$[\text{Ni}(\text{TP})_2\text{B}]$	-	Square pyramidal
$[\text{Ni}(\text{CPT})_2]$	-	Square planar
$[\text{Cu}(\text{CPT})(\text{TPH})\text{B}]\cdot\text{H}_2\text{O}$	-	Tetrahedral or linear, polymeric
$[\text{Cu}(\text{CPT})(\text{CPTH})]\cdot\text{H}_2\text{O}$	-	Linear, polymeric.

Table IV.1

Analytical Data of the Complexes

Complexes	ANALYSES Found (Calcd) %				
	C	H	N	S	M
$[\text{Ni}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$	42.5 (42.9)	2.8 (3.2)	15.1 (14.7)	13.7 (13.4)	12.5 (12.2)
$[\text{Ni}(\text{TP})_2\beta\text{-(or } \gamma)\text{pic}]\cdot \text{H}_2\text{O}$	45.4 (45.9)	3.1 (3.2)	15.2 (14.8)	13.5 (13.6)	12.2 (12.3)
$[\text{Ni}(\text{TP})_2\text{Imid}]\cdot 2\text{H}_2\text{O}$	39.3 (38.9)	2.4 (2.2)	17.8 (18.1)	13.6 (13.8)	12.3 (12.5)
$[\text{Cu}(\text{TP})(\text{TPH})\text{Py}]\cdot \text{H}_2\text{O}$	43.6 (44.0)	3.1 (3.0)	14.8 (15.0)	13.6 (13.7)	13.5 (13.7)
$[\text{Cu}(\text{TP})(\text{TPH}, \text{Imid})]\cdot \text{H}_2\text{O}$	39.5 (40.0)	2.9 (2.7)	18.5 (18.6)	14.0 (14.2)	13.8 (14.0)
$[\text{Ni}(\text{CPT})_2]$	36.7 (36.5)	2.8 (3.0)	21.0 (21.3)	16.0 (16.2)	14.5 (14.6)
$[\text{Cu}(\text{CPT})(\text{CPTH})]\cdot \text{H}_2\text{O}$	34.8 (34.5)	3.3 (3.6)	19.8 (20.1)	15.3 (15.3)	15.1 (15.2)

Table IV.2

Comparison of TPH and its Nickel Complexes
with respect to IR Band Position† (cm⁻¹)

TPH	4		
	1	2	3
	[Ni(TP) ₂ Py].2H ₂ O	[Ni(TP) ₂ pic].H ₂ O	[Ni(TP) ₂ Imid].2H ₂ O
3200	3330(m), 3220(vw),	3410, 3313,	3400, 3320,
3100(w)	3170	3215, 2990	3220, 2920,
			2850
1765	1750, 1725	1750(w), 1730	1745, 1730
	1625*	1625*	1635*
1560	1552, 1535,	1545, 1500*(m)	1550, 1500*
	1500*(m)		
1440	1420	1472*(m), 1462*(m)	1440
		1432	
1350	1375	1372	1375
1310(b)	1315	1315	1315
1248, 1225	1285(w), 1220,	1222(b), 1195(b)	1290, 1220,
1193	1200		1200
1140(b)	1150(w), 1107	1104, 1115(w)	1155(m), 1102
1053, 1010	1080, 1050,	1058, 1025*,	1058, 1025*,
	1010*(m), 998	1000	998
966(m)	965	-	960

...contd.

Table IV.2 (contd.)

1	2	3	4
894, 840	913, 885, 875, 860(m), 840, 825(m)	916, 895(w), 880(m), 860, 830	915, 895(w), 880(w), 860, 830
750	768(m), 745	758(w), 745	765(sh), 748
702, 690, 663	708(sh), 690, 660(m)	690, 663(w)	710(w), 690, 660(w)
620	600	622(w), 610(w)	605(w)
580(w)	572(m)	-	568(w)
554	-	548(m)	540(w)
480	448(m) 340(b,m)	490 400	480(w) 430(w)
330	300(w)	385, 325	390(w), 342(b,m), 300(vw)

*Major additional bands; m = medium; w = weak; vw = very weak; b = broad;

sh = shoulder.

#Sharpness and intensity may be seen from the spectra.

Electronic Spectral Bands of Complexes[‡] (recorded in chloroform) and their Assignments

Compounds	Position of the absorption bands, R_{\max} , (cm ⁻¹)	Assignments
[Ni(TP) ₂ Py].2H ₂ O	7092	$\nu_1, d_z^2 \rightarrow d_{x^2-y^2}$
	8333(m,b)	-
	11111(b)	$d_{xy} \rightarrow d_{x^2-y^2}$
	18180(b)	-
	22222	Charge transfer
	27400	Charge transfer
	35461	Intraligand
[Ni(TP) ₂ β -(or γ -)pic].H ₂ O	7067	$\nu_1, d_z^2 \rightarrow d_{x^2-y^2}$
	11111(b)	$d_{xy} \rightarrow d_{x^2-y^2}$
	21980	Charge transfer
	27027	Charge transfer
	34722	Intraligand
[Ni(CPT) ₂] [‡]	17857	$d_{x^2-y^2} \rightarrow xy$
	21277	$xz \rightarrow xy$
	26320	Charge transfer, [L(π) \rightarrow d _{xy}]
	35714	Intraligand, [L(π) \rightarrow L(π^*)]
[Cu(TP)(TPH)Py].H ₂ O [‡]	35714	Intraligand
	41667	Intraligand

[‡]Only representative complexes are included; [‡] Spectra recorded in nujol mull; b = broad; w = weak; m = medium.

LEGEND TO THE FIGURES

Fig. IV.1 Infrared Spectra

1. $[\text{Ni}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$
2. $[\text{Ni}(\text{TP})_2\cdot\text{Imid}]\cdot 2\text{H}_2\text{O}$
3. $[\text{Ni}(\text{CPT})_2]$
4. $[\text{Ni}(\text{TP})_2\text{Pic}]\cdot\text{H}_2\text{O}$
5. $[\text{Cu}(\text{CPT})(\text{CPTH})]\cdot\text{H}_2\text{O}$
6. $[\text{Cu}(\text{TP})(\text{TPH})\text{Py}]\cdot\text{H}_2\text{O}$

Fig. IV.2 NIR, UV-Visible Spectra

- A. $[\text{Ni}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$
- B. $[\text{Ni}(\text{TP})_2\beta\text{-Pic}]\cdot\text{H}_2\text{O}$
- C. $[\text{Ni}(\text{TP})_2\cdot\text{Imid}]\cdot 2\text{H}_2\text{O}$
- D. $[\text{Cu}(\text{TP})(\text{TPH})\text{Py}]\cdot\text{H}_2\text{O}$
- E. $[\text{Ni}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$
- F. $[\text{Ni}(\text{TP})_2\beta\text{-Pic}]\cdot\text{H}_2\text{O}$

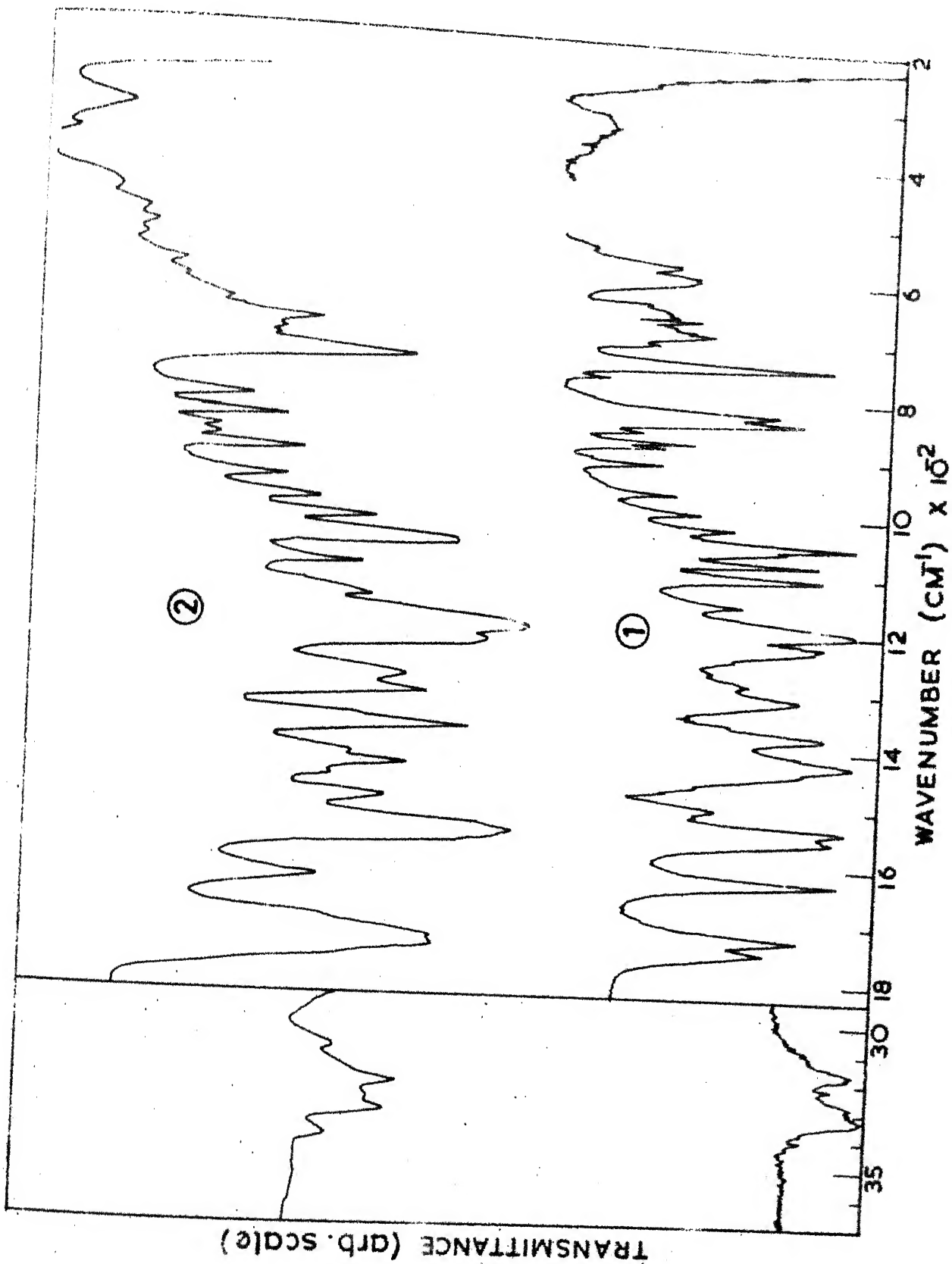


FIG. IV.1

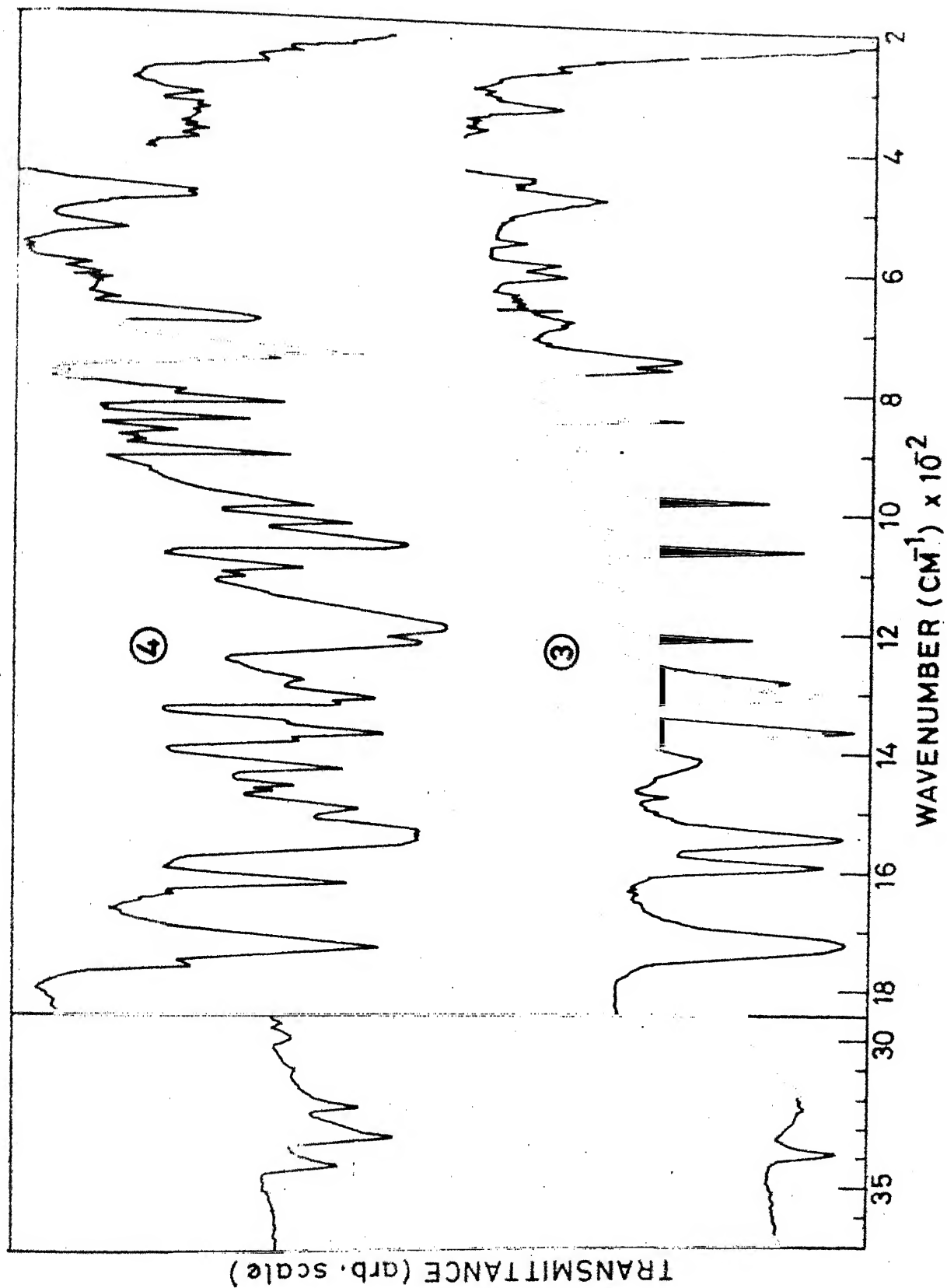


FIG. IV.1

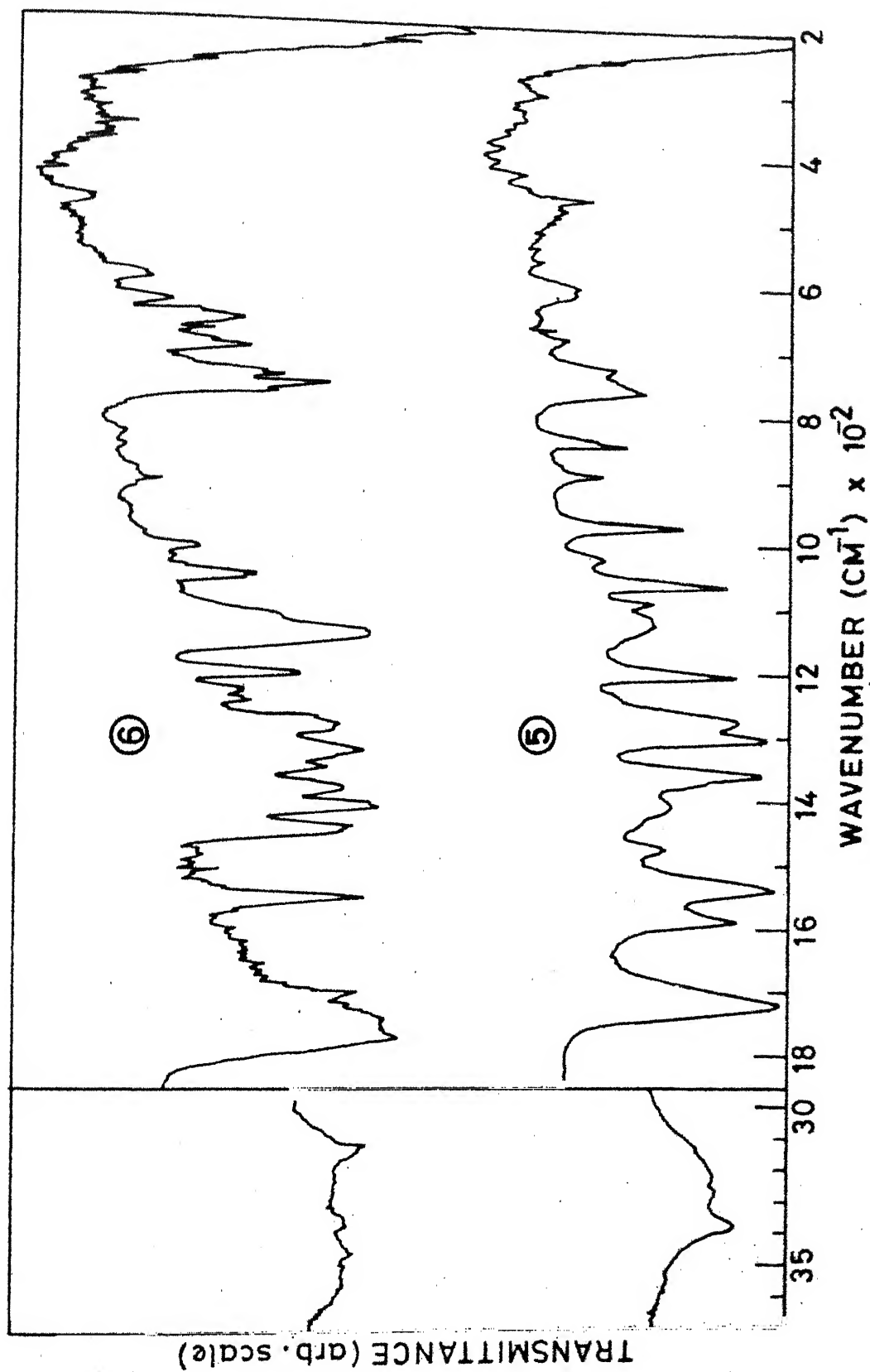


FIG. IV.1

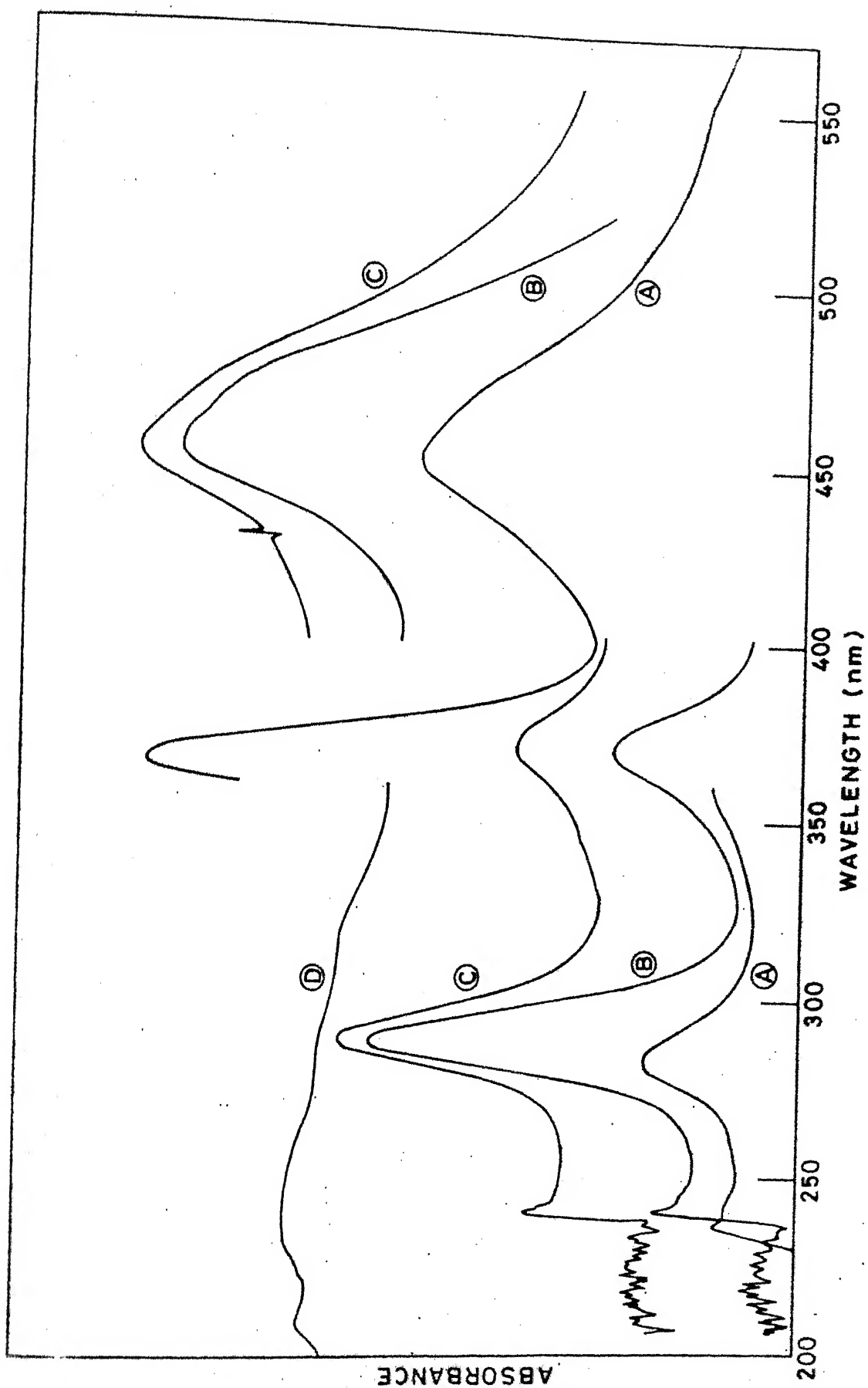


FIG. IV.2

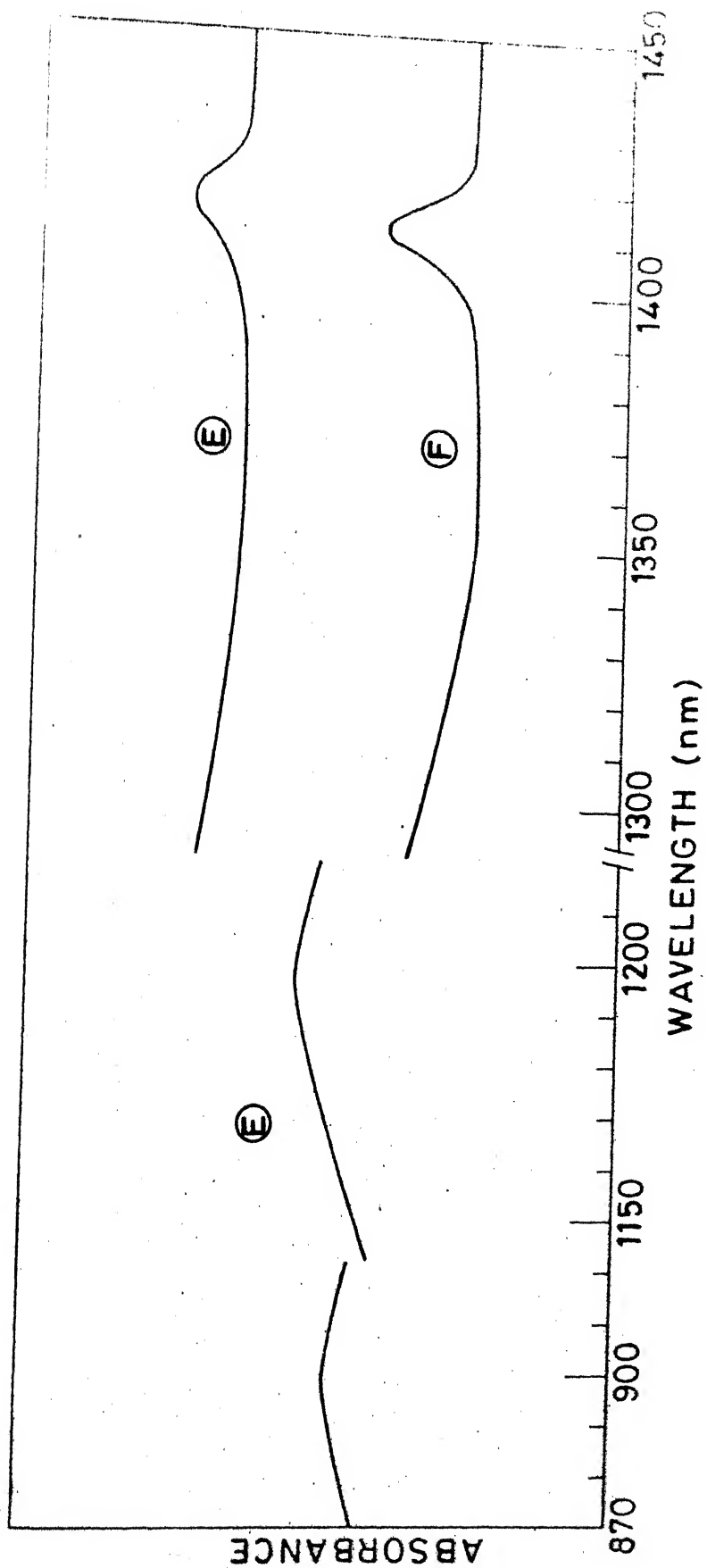


FIG. IV. 2

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CHAPTER V

REACTIONS OF 2-THIOPYRROLE-1,2-DICARBOXIMIDE AND N-CARBAMOYL-PYRROLE-2-THIOCARBOXAMIDE WITH SOME OF THE SECOND AND THIRD ROW TRANSITION METAL IONS AND THEIR COMPLEXES

In preceding chapters, the syntheses and the tentative structures of the complexes of a few first row transition metal ions with TPH and CPTH have been described. Attempts to synthesize complexes with the rest of the elements of first transition series met with unsuccessful results. Since the results were so fascinating, especially with cobalt, that we were tempted to

synthesize complexes of second and third row transition metal ions with TPH and CPTH. This chapter describes the preparation and properties of ruthenium, rhodium, palladium and platinum complexes of TPH and CPTH. Their structures were derived by analytical, magnetic susceptibility and spectral (IR, UV-visible) studies.

EXPERIMENTAL

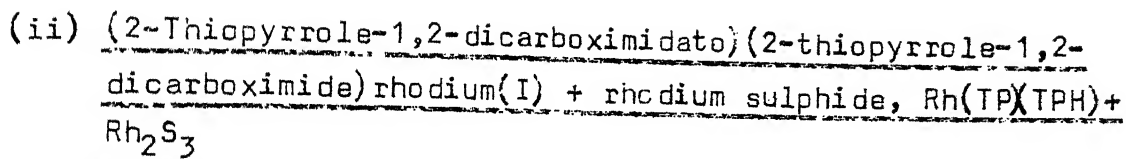
The chemicals used were either chemically pure or AnalaR grade. Ligands, TPH and CPTH, were synthesized by the methods as described in Chapter II. $\text{RhCl}(\text{PPh}_3)_3$ ¹ and $\text{Pd}(\text{PPh}_3)_4$ ² were prepared by the literature methods.

Preparation of Metal Complexes

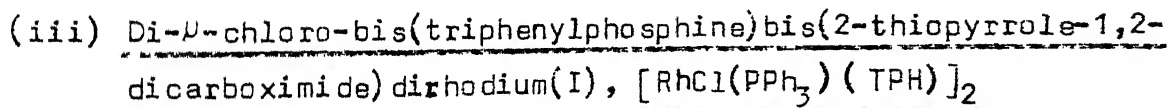
(i) Bis(2-thiopyrrole-1,2-dicarboximidato)ruthenium(II), $\text{Ru}(\text{TP})_2$

An aqueous solution (25 ml) of hydrated ruthenium trichloride (0.26 g, 1 mmol) was added to an ethanolic solution (25 ml) of the ligand (0.35 g, 2.3 mmol). The amount of the ligand taken was slightly more than that required from the stoichiometric ratio. The resulting solution was refluxed on a water bath for about ten minutes, whereby a black brown complex precipitated out. It was separated by centrifugation, washed successively several times with water, ethanol and

diethyl ether. It was dried under vacuum. The complex did not melt upto 280°C .



25 ml of the filtered ethanolic solution of hydrated rhodium trichloride (0.26 g, 1 mmol) was added to 25 ml of an ethanolic solution of the ligand (0.35 g, 2.3 mmol), whereupon the ^{Colour of the} solution got intensified. The resulting solution was slowly evaporated to almost dryness on a water bath. The pasty mass was treated with an excess of water and digested on a water bath. The residue, thus obtained, was separated by centrifugation, washed several times with water, small amounts of ethanol and finally with diethyl ether. It was dried under vacuum. The analytical data indicated the final product as a mixture of 90% $\text{Rh}(\text{TP})(\text{TPH})$ and 10% of Rh_2S_3 .



25 ml of a dichloromethane solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.46 g, 0.5 mmol) was added to 25 ml of the dichloromethane solution of the ligand (0.1 g, 0.66 mmol). The colour of the solution was changed to reddish brown immediately. Thereafter the solution was refluxed on a water bath for about fifteen minutes. The resulting solution was evaporated to almost

dryness. The pasty mass, thus obtained, was dissolved in methanol and filtered. Petroleum ether (40-60°) was added to the filtrate to start the precipitation. The solution was cooled in a refrigerator. The complex, thus precipitated, was separated by centrifugation, washed with petroleum ether and dried in vacuo. The compound was reprecipitated by dissolving it in either CH_2Cl_2 or MeOH and adding petroleum ether (m.p. 207°).

(iv) a. Bis(2-thiopyrrole-1,2-dicarboximidato)palladium(II),
 $[\text{Pd}(\text{TP})_2]$

25 ml of a solution of palladium chloride (0.18 g, 1 mmol) (dissolved in dilute hydrochloric acid) was added with stirring to a 25 ml of an ethanolic solution of the ligand (0.31 g, 2 mmol). The mixture was further stirred for about five minutes, whereby a brown complex, $\text{Pd}(\text{TP})_2$, was precipitated out. It was suction filtered, washed several times successively with dilute hydrochloric acid (ca. 10^{-3} M), distilled water, ethanol, diethyl ether and dried in vacuo.

b₁. Reaction of $[\text{Pd}(\text{DMSO})_2\text{Cl}_2]$ ³ with TPH

0.1 g of palladium chloride was dissolved in 1 ml of dimethyl sulphoxide and the resulting solution was treated with diethyl ether whereupon yellow crystals of $[\text{Pd}(\text{DMSO})_2\text{Cl}_2]$ were obtained. The complex was filtered and redissolved in minimum quantity of DMSO. The resulting solution was treated with

25 ml of an ethanolic solution of the ligand (0.2 g, 1.3 mmol) yielded a product identical to that described in (iv)a.

b₂. In case, the DMSO solution of palladium chloride, prepared as described in the preceding paragraph, was treated with the ligand solution (in DMSO) and the resulting mixture was refluxed for about half an hour, a black compound was obtained which was separated by filtration and analysed as PdS along with some other product. The filtrate, obtained after the separation of the black compound, was evaporated to near dryness on a water bath and the pasty mass was treated with methanol whereby more black compound appeared which was separated by filtration. The filtrate was reevaporated to almost dryness and the residue was extracted from dichloromethane. Slow evaporation of the dichloromethane solution yielded a yellow product which was identified as the oxidation product of the ligand (refer to Chapter II).

c. Reaction of $[\text{Pd}(\text{DMF})_2\text{Cl}_2]$ with TPH

The reactions described in (iv)b₁ and (iv)b₂ were repeated by using DMF in place of DMSO. The product obtained by the procedure (iv)b₁ was $\text{Pd}(\text{TP})_2$ and that by (iv)b₂ was the oxidation product of the ligand.

d. Reaction of $\text{Pd}(\text{PPh}_3)_4$ with TPH. Preparation of $[\text{Pd}(\text{PPh}_3)_2(\text{TPH})_2]$

0.1 g of the freshly prepared $\text{Pd}(\text{PPh}_3)_4$ was dissolved in

30 ml of dichloromethane and the solution was added with stirring to a 25 ml ethanolic solution of ligand (0.3 g, 2 mmol). On keeping the mixture for few hours, yellow complex was precipitated out which was separated by filtration, washed several times successively with dichloromethane, ethanol and diethyl ether. It was dried in vacuo. The analyses of the product was best approximated as $[\text{Pd}(\text{PPh}_3)_2(\text{TPH})_2]$.

(v) Bis(2-thiopyrrole-1,2-dicarboximidato)platinum(II) monohydrate
 $[\text{Pt}(\text{TP})_2] \cdot \text{H}_2\text{O}$

25 ml of an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ was treated with 25 ml ethanolic solution of the ligand in stoichiometric ratio. The solution was heated for about half an hour on a boiling water bath whereby a brown coloured precipitate, $\text{Pt}(\text{TP})_2 \cdot \text{H}_2\text{O}$, was formed. It was allowed to stand at room temperature for about half an hour and separated by centrifuging it. It was washed several times successively with water, small quantity of ethanol, diethyl ether and dried in vacuo. It was reprecipitated by dissolving it in ethanol and precipitating by water.

(vi) Dichlorobis(N-carbamoylpyrrole-2-thiocarboxamide)-ruthenium(II), $[\text{Ru}(\text{CPTH})_2\text{Cl}_2]$

This compound was prepared by the method similar to that described in (i) except that 1 ml of dil. HCl was added to the

metal chloride solution (25 ml) and CPTH was used in place of TPH.

(vii) (N-carbamoylpyrrole-2-thiocarboxamidato)(N-carbamoylpyrrole-2-thiocarboxamide)rhodium(I), [Rh(CPT)(CPTH)]

The complex was prepared by the same method as described in (ii) except that CPTH was used in place of TPH.

(viii) Bis(N-carbamoylpyrrole-2-thiocarboxamidato)palladium(II), [Pd(CPT)₂]

The procedure for the preparation of the complex was similar to the one described in (iv)a except that CPTH was used in place of TPH.

(ix) Bis(N-carbamoylpyrrole-2-thiocarboxamidato)platinum(II), [Pt(CPT)₂]

The complex was prepared by the method as described in (v) except that CPTH was used in place of TPH.

ANALYSES

Rhodium was analysed by taking a known weight of the sample and decomposing it with a mixture of concentrated H₂SO₄ and concentrated HNO₃ (1:1). The solution was evaporated to almost dryness and the residue was extracted with water. The process of decomposition with the concentrated acid was

repeated three to four times for ensuring complete decomposition. Rhodium was estimated as $[\text{Co}(\text{NH}_3)_6][\text{Rh}(\text{NO}_2)_6]$ in the solution.⁴

For the estimations of palladium and platinum,⁵ samples were decomposed in aquaregia. In phosphorus containing complexes, the decomposition was carried out as described in the foregoing paragraph for the estimation of rhodium. The excess nitric acid was removed by repeated evaporation with HCl acid. The residue was taken in dil. HCl (10^{-3} M) and palladium was estimated as $\text{Pd}(\text{DMG})_2$ and platinum, as $[(\text{NH}_4)_2\text{PtCl}_6]$ in the solution.

Chloride, sulphur and phosphorus were estimated gravimetrically by the methods as described in Chapter II. Carbon, hydrogen and nitrogen were determined by the microanalytical section of the Indian Institute of Technology, Kanpur. The analytical data are presented in Table V.1.

Magnetic susceptibility measurements were carried out by a standard Gouy balance. All the complexes reported in this chapter are diamagnetic. Infrared, UV-Visible Spectra were recorded in the same way as described in previous chapters.

RESULTS AND DISCUSSION

The complexes are, in general, air stable, slightly soluble in most of the organic solvents except $[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2$ which was found to be quite soluble. The analytical data and

the preferred geometries which the metal ions generally adopt suggested that the ligands in some complexes acted as bidentate while in others, as monodentate. Their infrared spectra were recorded in the region $4000-200\text{ cm}^{-1}$ to decide the bonding sites of the metal ions in the ligand. As reported in the previous chapters also, the IR spectra of the complexes were quite complicated because of the extensive mixing of various modes of vibrations in the ligand. However, the spectra of the ligands and those of the complexes were compared and the systematic shifts in the various band positions were recorded which aided in deciding tentatively the donor sites of the ligand molecules. The systematic shifts of the positions of the bands due to various modes in the complexes are grouped under the following headings for the sake of convenience in discussion.

TPH Complexes of Ru(II), Rh(I), Pd(II) and Pt(II)

The shifts in the band positions in the spectra of the complexes of these metal ions have been found to be similar. The following are the general observations in their spectra.

(i) The ligand band at 3200 cm^{-1} assigned to $\nu(\text{NH})$ disappeared in the spectra of all the complexes suggesting the deprotonation of the ligand. 27

(ii) The amide band I ($\nu_{\text{C=O}}$) in the complexes was shifted in some spectra to the lower wavenumber side ($\sim 30\text{ cm}^{-1}$)

indicating the involvement of carbonyl oxygen in bond formation.⁶

(iii) The position of the thioamide bands having contribution from $\nu(\text{C}=\text{N})$, $\delta(\text{NH})$ and those of amide bands in the region⁷ 1500 cm^{-1} to 1000 cm^{-1} either did not shift or the shifts were too small to draw any definite conclusions from the direction of shifts.

(iv) The thioamide band (IV)⁸ (840 cm^{-1}) present in the ligand was shifted slightly towards higher wavenumbers suggesting the noninvolvement of thiocarbonyl sulphur in the bond formation. In some of the complexes like Ru(II), the position of $\nu(\text{C}=\text{S})$ band shifted to slightly lower wavenumbers suggesting thiocarbonyl sulphur also as donor site. It appears that in these complexes, the thiocarbonyl sulphur is also participating in bond formation, making the ligand behave as tridentate and giving an octahedral geometry around the metal.

(v) New bands of weak to medium intensity in the region 300 cm^{-1} to 500 cm^{-1} appeared which may be assigned to the coupled vibrations due to $\nu(\text{M}-\text{S})$, $\nu(\text{M}-\text{O})$ or $\nu(\text{M}-\text{N})$.⁹

Thus, putting together the arguments discussed in the foregoing paragraphs, it may be concluded that the bonding of the metal ions in the complexes is taking place through the nitrogen and oxygen of $-\text{C}(\text{S})-\text{NH}-\text{C}(\text{O})-$ moiety. Diamagnetism of the complexes suggested that the ligand acted as reducing

agent towards ruthenium and rhodium metal ions giving Ru(II) and Rh(I) complexes, respectively.

Since the complexes of ruthenium are highly insoluble, the polymeric structure could be suggested for them. The slight solubility of the other complexes suggest that these are also polymeric but the degree of polymerisation might be relatively less. The STRUCTURE I may, therefore, be suggested for the complexes.

The complex, $[RuCl(TPH)(PPh_3)]_2$, similarly, may be assigned to possess the square planar geometry with chloride bridges. Thus, ligand is supposed to behave unidentate with oxygen of the carbonyl group involved in the bond formation. The bonding in this complex is as shown in STRUCTURE II. The spectra of the DMSO and DMF complexes of palladium showed the formation of a mixture of products since most of the characteristic frequencies of the ligand were absent.

CPTH Complexes of Ru(II), Rh(I), Pd(II) and Pt(II)

The major shifts in the band positions in the infrared spectra of the complexes with CPTH are as follows:

(i) 3200 cm^{-1} band assigned to $\nu(\text{NH})$ disappeared in the Pt and Pd complexes suggesting deprotonation of the NH group. In the spectra of Rh(I) and Ru(II) complexes, this band did not disappear indicating that -NH bond remained intact in the complexes.

(ii) The position of the amide band (I) due to $\nu(\text{CO})$ shifted to lower wavenumbers (25 cm^{-1}) confirming the carbonyl oxygen as donor site for the bond formation with the metal ion.

(iii) The position of the thioamide band (IV) having major contribution from $\nu(\text{C=S})$, remained practically stationary ($\pm 5 \text{ cm}^{-1}$) suggesting that the thiocarbonyl sulphur may be involved in the bond formation.

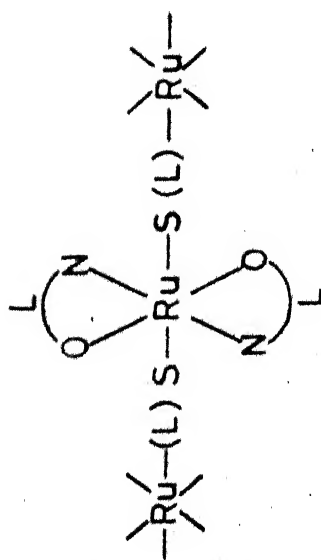
(iv) The shifts in the thioamide and amide band positions between 1500 cm^{-1} and 1200 cm^{-1} were erratic and, therefore, no inference could be drawn.

On the basis of the above shifts in the IR band positions and assuming the preferential geometries which these metal ions assumed in their complexes, the bonding in these complexes could be shown as STRUCTURE III.

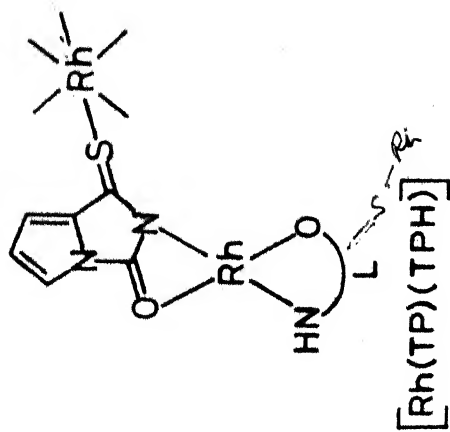
Magnetic Properties of the Complexes

All the complexes were found to be diamagnetic suggesting that the Ru(III) and Rh(III) have been reduced by the ligand to Ru(II) and Rh(I), respectively after complex formation. 4d & 5d transition metals generally form low spin complex because of larger size of their orbitals compared to that of 3d and produce less interelectronic repulsion. It will result ⁱⁿ ~~into~~ the large splitting of d orbitals and hence the pairing is formed.¹⁰ The large value of spin-orbit coupling constant

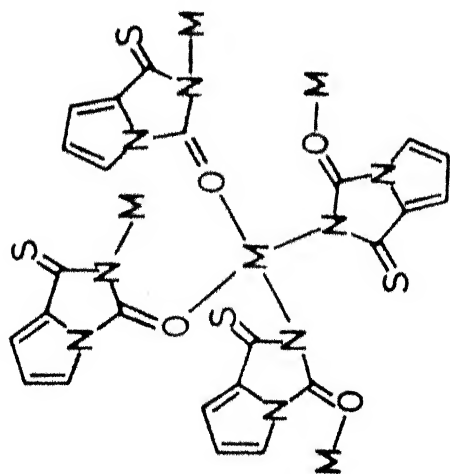
STRUCTURE I



$[Ru(TP)_2]$



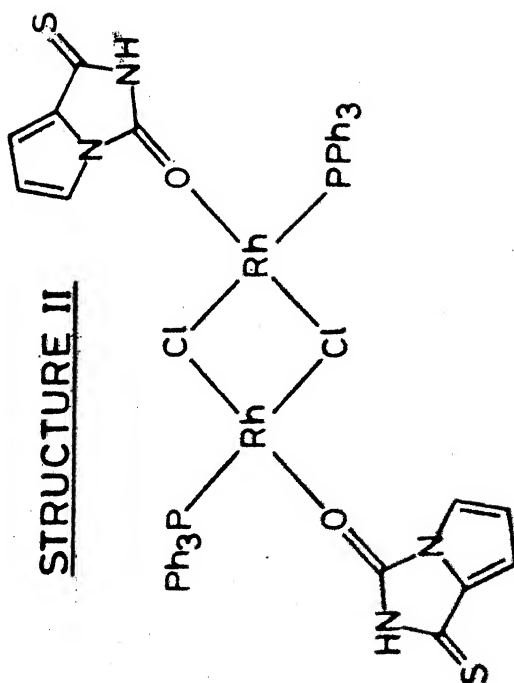
$[Rh(TP)(TPH)]$

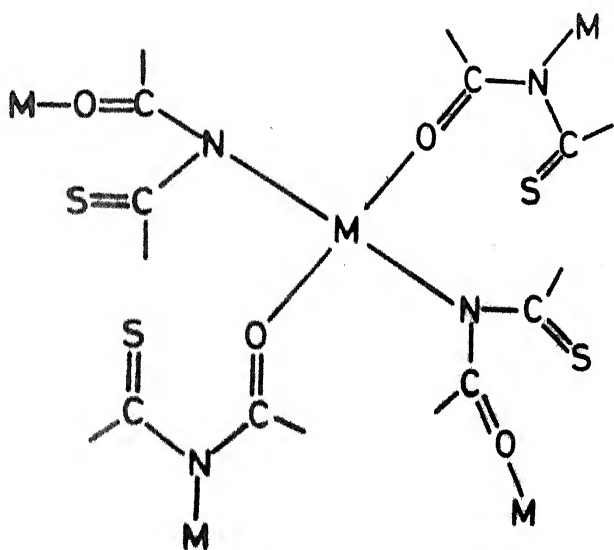


M = Pd and Pt

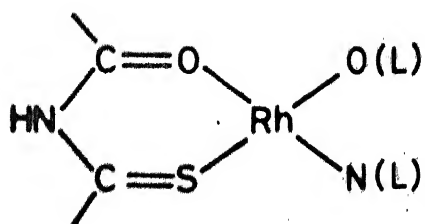
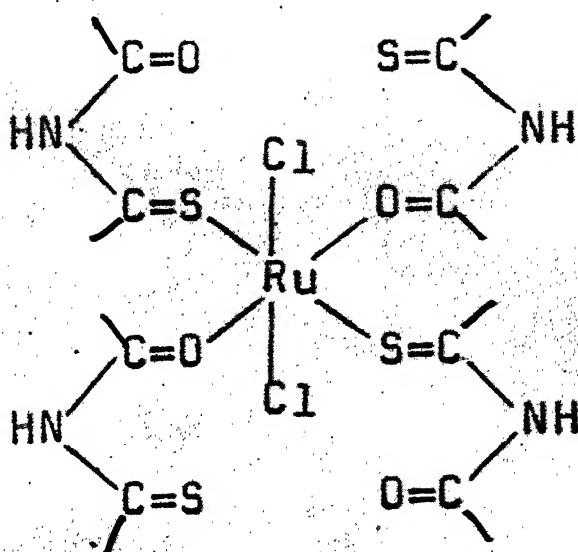
L = Indicates the ligand

STRUCTURE II



STRUCTURE III

(M = Pt and Pd)

 $[Rh(CPT)(CPTH)]$ 

or other isomers

 $[Ru(CPTH)_2Cl_2]$

for heavier metals also caused spin pairing and thus resulting in ~~the~~ low spin behaviour.

Electronic Spectra

The spectra of the complexes were recorded in nujol owing to the lack of solubility in suitable noncoordinating solvents. Though the complexes were soluble in pyridine but it has not been used because of the possibility of the change of geometries of the complexes in solution.¹¹ Near IR region did not show any band while in visible region the broad bands appeared. In some cases the maxima ~~is~~ ^{are} quite defined while in others it is difficult to decide the maxima. In the UV region also the spectra of the complexes did not show any well defined maxima in nujol possibly because of large concentration of the compound.

In most of Ru(II) complexes, ruthenium preferentially has ~~an~~ ^{an} octahedral geometry.¹² If one assumes an octahedral environment around the metal ion in a strong ligand field, one should expect four bands, two spin allowed corresponding to the transition $^1A_{1g}$ to $^1T_{1g}$ and $^1T_{2g}$ and two spin forbidden bands from $^1A_{1g}$ to $^3T_{1g}$ and $^3T_{2g}$. If the symmetry is lowered from O_h , T_{1g} and T_{2g} levels further split up giving more levels and thus the number of bands arising out of the transitions between these levels will increase. The TPH complex of ruthenium, $Ru(TP)_2$, showed only one well defined broad band at 395 nm

(25319 cm^{-1}) which may be assigned to $^1A_{1g}$ to $^1T_{2g}$ spin allowed transition. Other low energy transitions were probably masked by the tail of the band.

The spectra of the CPTH complex, however, showed a very broad band, whose maximum was approximated around 480 nm (20833 cm^{-1}), was assigned to $^1A_{1g}$ to $^1T_{2g}$ transition.

The spectra of $[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2$, recorded in chloroform, showed three bands at 365 nm (27400 cm^{-1}), 310 nm (32258 cm^{-1}) and 280 nm (35714 cm^{-1}). The first two bands were present in the spectrum of the ligand but the positions of these bands were shifted towards lower wavelength in the spectra of the complex indicating the metal interaction with the ligand. These bands are, therefore, assigned to intraligand transitions. The higher energy band at 35714 cm^{-1} is possibly a characteristic band of triphenylphosphine. No d-d bands were observed in the spectrum probably because they were masked by the strong C.T. bands. The spectrum of the rhodium complex of CPTH showed a broad absorption band with a maximum at about 440 nm (22727 cm^{-1}). In square planar rhodium complexes (d^8 system), three spin allowed d-d transitions are anticipated. Besides these, the spectrum should show three spin forbidden singlet-triplet transitions from $^1A_{2g}$ to $^3A_{2g}$, $^3B_{1g}$ and 3E_g , respectively. The 22727 cm^{-1} band of Rh(I) complex is present relatively at high energy side. Generally, Rh(I) square planar complexes¹³ absorb in the 400 nm region because of the transition $^1A_{2g}$ to 1E_g , 440 nm band is,

therefore, assigned to this transition.

The visible spectra of the complex, $\text{Pd}(\text{TP})_2$, showed maximum at 470 nm (21270 cm^{-1}) and that of $\text{Pt}(\text{TP})_2$ at 520 nm (19231 cm^{-1}). The literature value^{14,15} of the absorption maxima in the visible region for the square planar complexes of palladium and platinum falling in this region are assigned to $x^2-y^2 \rightarrow xy$ ($^1A_{1g} \rightarrow ^1B_{1g}$) transition. The band at 21277 cm^{-1} and 19231 cm^{-1} of palladium and platinum complexes, respectively is, therefore, assigned to $x^2-y^2 \rightarrow xy$ transition.

Thus, on the basis of the analytical, magnetic and spectroscopic data, the following tentative geometries have been assigned to the complexes:

$[\text{Ru}(\text{TP})_2]$, $[\text{Ru}(\text{CPTH})_2\text{Cl}_2]$	- Octahedral
$[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2$, $[\text{Rh}(\text{TP})(\text{TPH})]$, $[\text{Rh}(\text{CPT})(\text{CPTH})]$	- Square planar
$\text{Pd}(\text{TP})_2$, $\text{Pt}(\text{TP})_2$, $\text{Pd}(\text{CPT})_2$, $\text{Pt}(\text{CPT})_2$	- Square planar

Table V.1

Analytical Data of the Complexes

Complex	ANALYSIS - Found(Calcd) %						
	C	H	N	S	M	X	P
[Ru(TP) ₂]	35.2 (35.5)	1.7 (1.5)	13.7 (13.8)	16.0 (15.8)	- -	- -	- -
90%[Rh(TP)(TPH)] + 10%[Rh ₂ S ₃]	32.5 (32.8)	1.8 (1.5)	15.1 (15.3)	17.4 (17.1)	27.9 (28.6)	- -	- -
[RhCl(PPh ₃)(TPH)] ₂	52.5 (51.1)	3.0 (3.3)	5.2 (5.1)	6.0 (5.8)	18.1 (18.6)	6.1 (6.4)	5.8 (5.6)
[Pd(TP) ₂]	35.0 (35.3)	1.5 (1.3)	14.2 (13.7)	15.5 (15.7)	26.2 (26.0)	- -	- -
[Pt(TP) ₂].H ₂ O	27.7 (28.0)	1.9 (1.6)	10.9 (10.7)	12.6 (12.4)	37.5 (38.1)	- -	- -
[Ru(CPTH) ₂ Cl ₂]	28.0 (28.2)	2.9 (2.7)	16.3 (16.5)	12.4 (12.6)	- -	13.7 (13.9)	- -
[Rh(CPT)(CPTH)]	32.5 (32.7)	2.7 (3.0)	19.3 (19.1)	14.3 (14.5)	22.9 (23.4)	- -	- -
Pd(CPT) ₂	32.2 (32.4)	2.4 (2.7)	18.8 (19.0)	14.2 (14.5)	23.8 (24.0)	- -	- -
[Pt(CPT) ₂]	27.4 (27.1)	2.1 (2.3)	15.5 (15.8)	12.1 (12.0)	36.2 (36.7)	- -	- -

Table V.2

UV-Visible Band Position for Some of the Complexes (nujol)

Complexes	Band position (cm^{-1}) (R_{max})	Assignment
$[\text{Ru}(\text{TP})_2]$	25319	$^1A_{1g} \rightarrow ^1T_{2g}$
$[\text{Ru}(\text{CPTH})_2\text{Cl}_2]$	20833	$^1A_{1g} \rightarrow ^1T_{2g}$
$[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2^*$	27400 32258	Arising due to ligand bands
$[\text{Rh}(\text{CPT})(\text{CPTH})]$	22727	$^1A_{2g} \rightarrow ^1E_g$
$[\text{Pd}(\text{TP})_2]$	21270	$x^2-y^2 \rightarrow xy$ $(^1A_{1g} \rightarrow ^1B_{1g})$
$[\text{Pt}(\text{TP})_2] \cdot \text{H}_2\text{O}$	19231	$x^2-y^2 \rightarrow xy$
$[\text{Pt}(\text{CPT})_2]$	20408	$x^2-y^2 \rightarrow xy$

* Spectra recorded in chloroform.

LEGEND TO THE FIGURES

Fig. V.1 Infrared Spectra

1. $[\text{Ru}(\text{TP})_2]$
2. $[\text{Ru}(\text{CPTH})_2\text{Cl}_2]$
3. $[\text{Rh}(\text{TP})(\text{TPH})]$
4. $[\text{Rh}(\text{CPT})(\text{CPTH})]$
5. $[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2$
6. $[\text{RhCl}(\text{PPh}_3)_3]$
7. $[\text{Pd}(\text{TP})_2]$
8. $[\text{Pd}(\text{CPT})_2]$
9. $[\text{Pt}(\text{TP})_2] \cdot \text{H}_2\text{O}$
10. $[\text{Pt}(\text{CPT})_2]$

Fig. V.2 UV-Visible Spectra

- A. $[\text{Ru}(\text{TP})_2]$
- B. $[\text{Rh}(\text{CPT})(\text{CPTH})]$
- C. $[\text{RhCl}(\text{PPh}_3)(\text{TPH})]_2$
- D. $[\text{Pd}(\text{TP})_2]$
- E. $[\text{Pt}(\text{TP})_2] \cdot \text{H}_2\text{O}$
- F. $[\text{Pt}(\text{CPT})_2]$

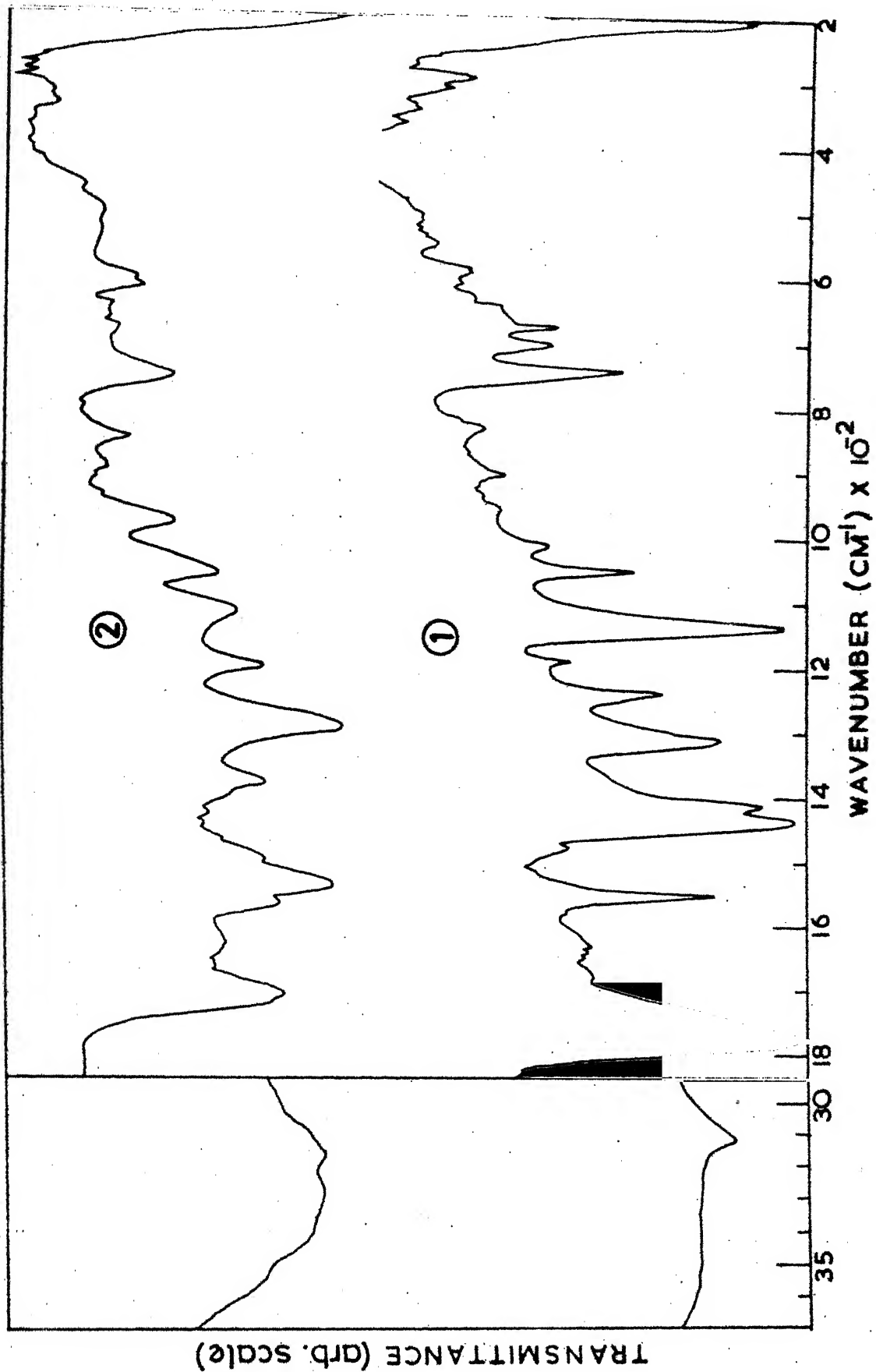


FIG. V.1

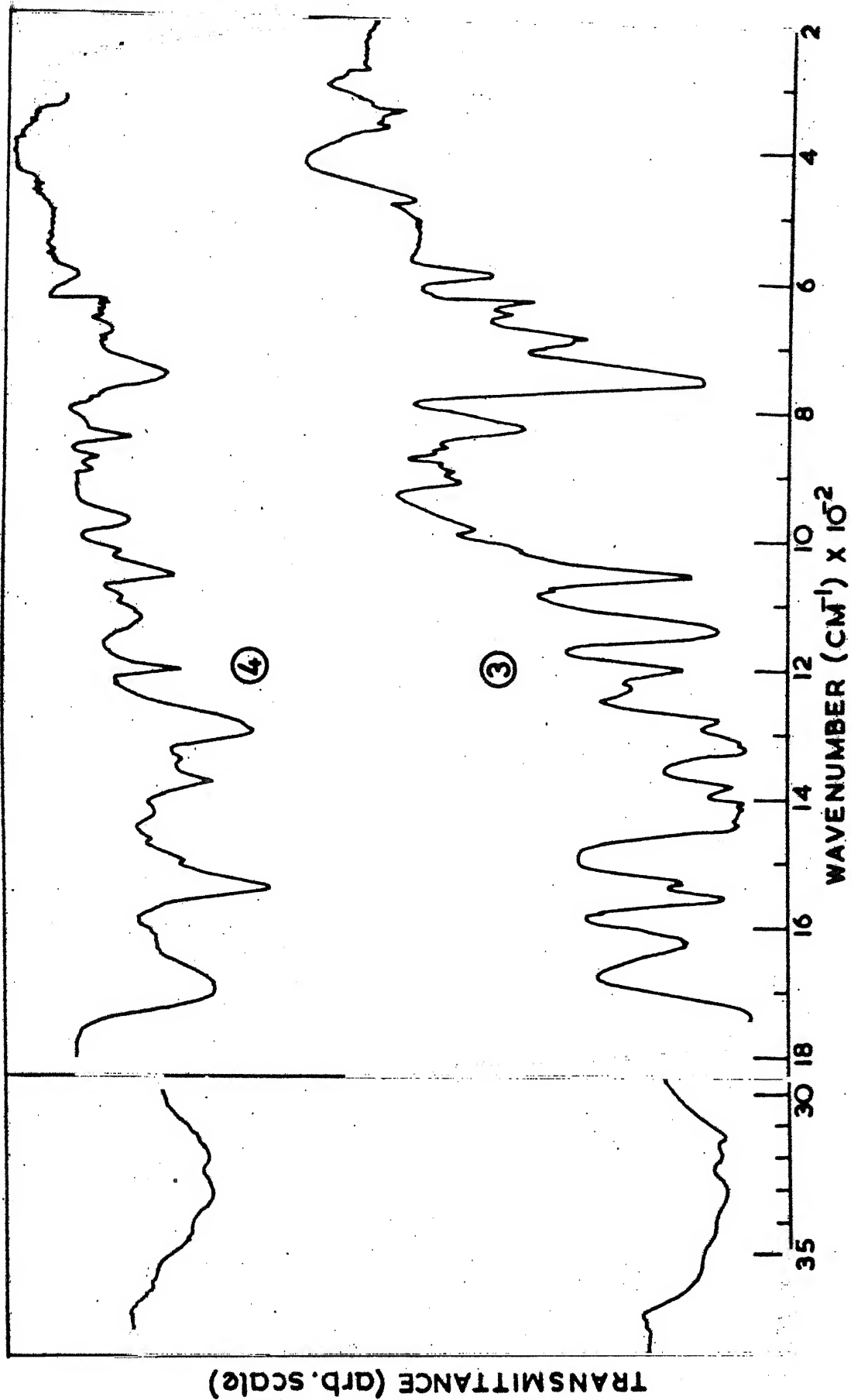


FIG. V.1

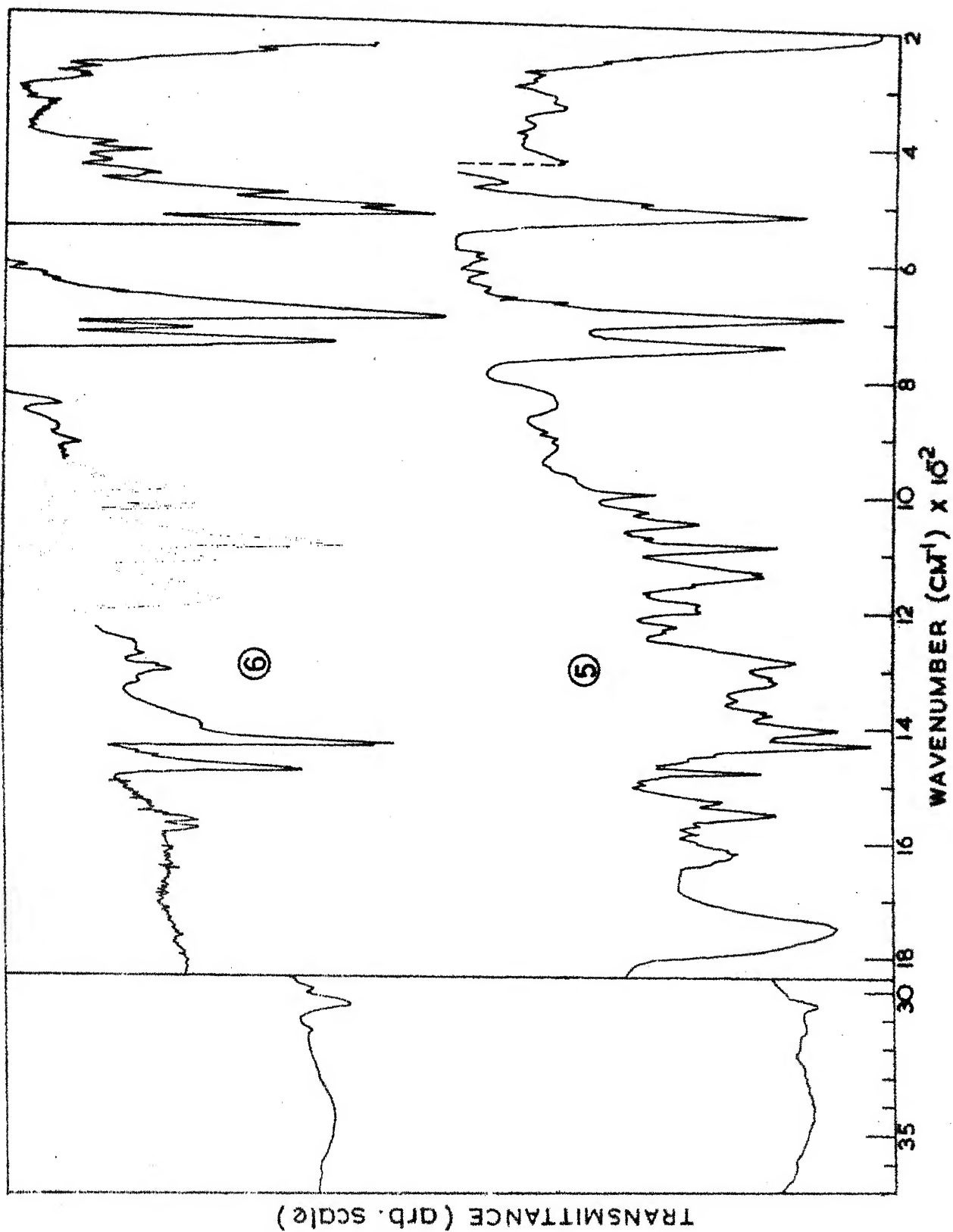


FIG. V.1

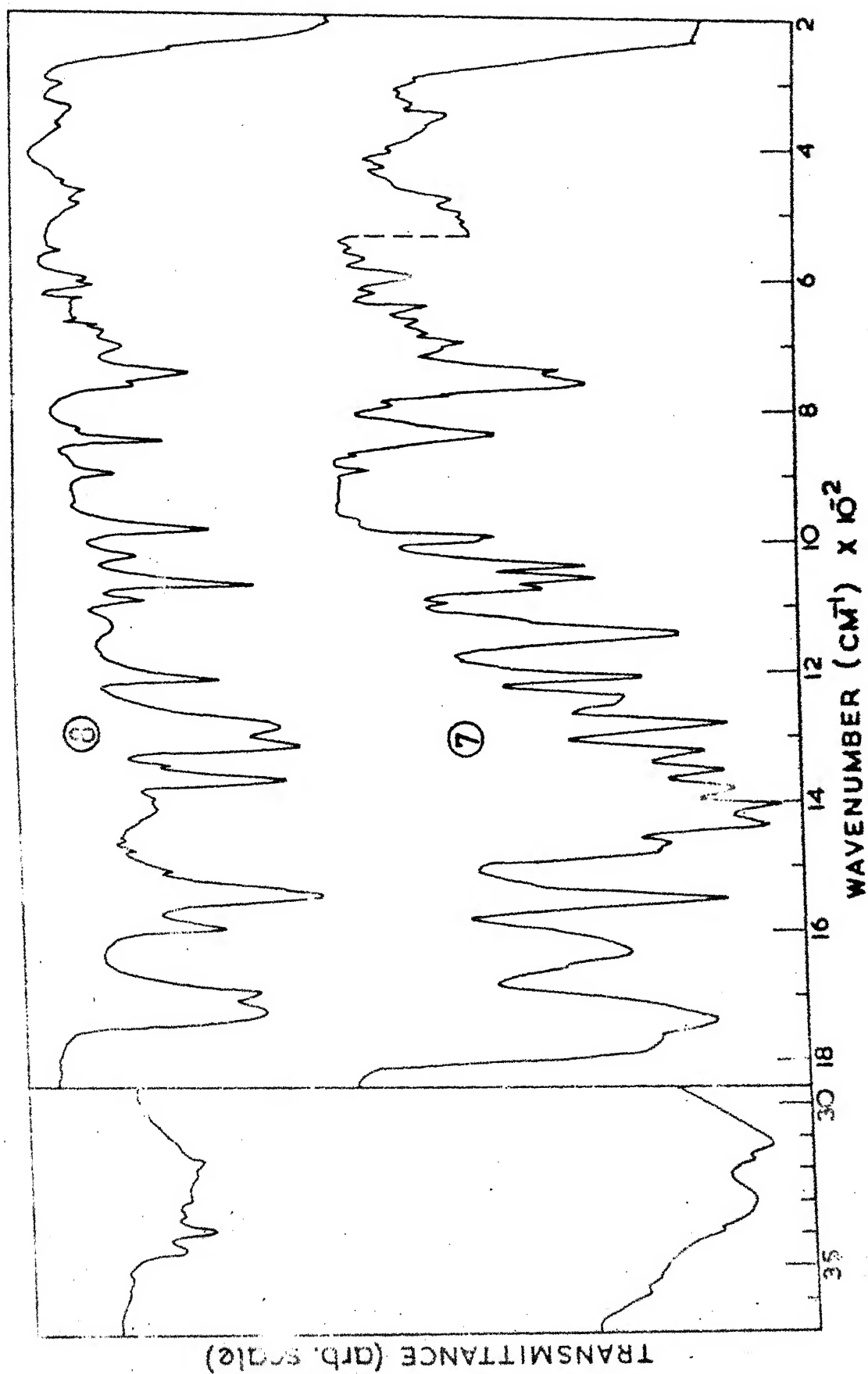


FIG. V.1

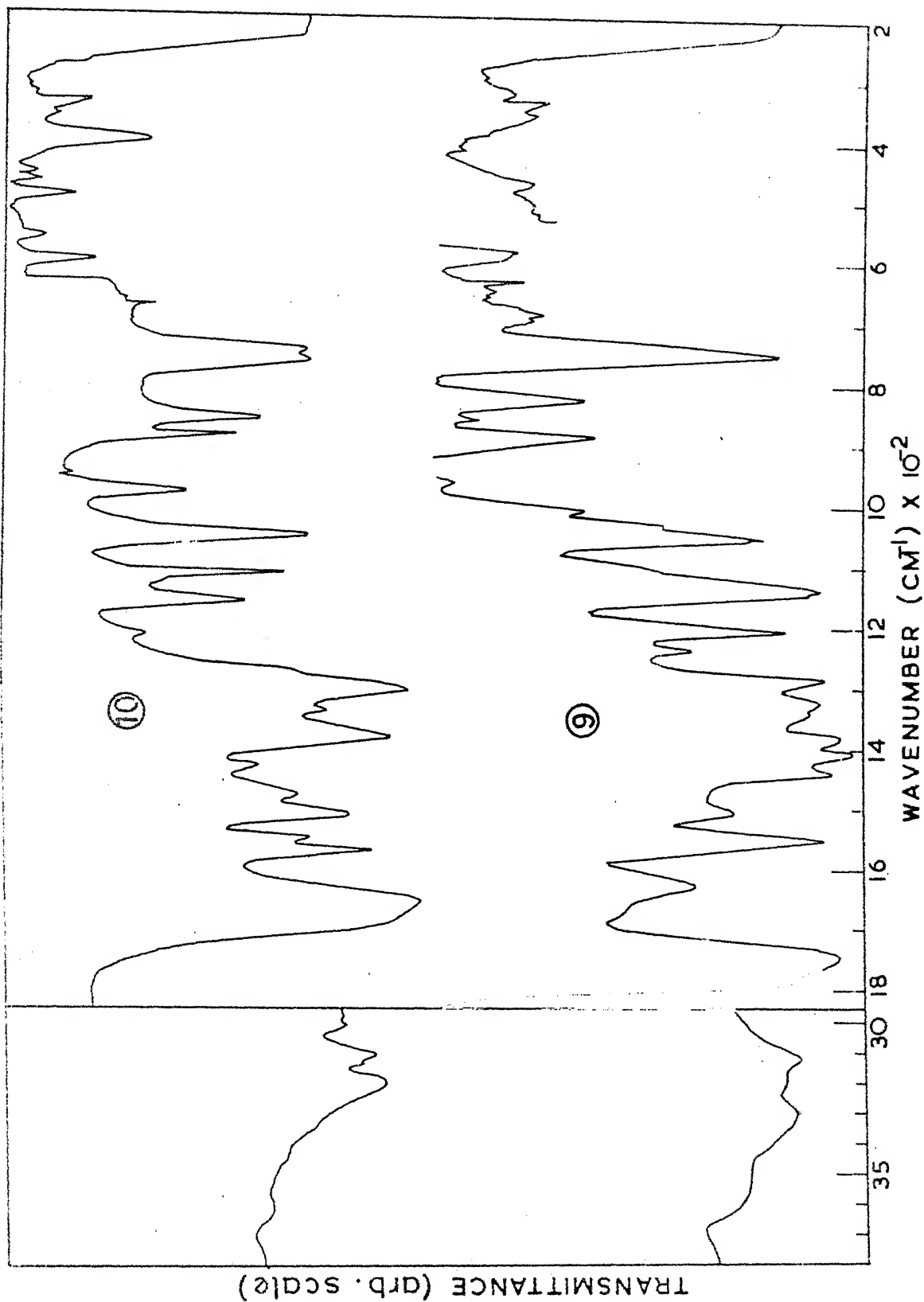


FIG. V.1

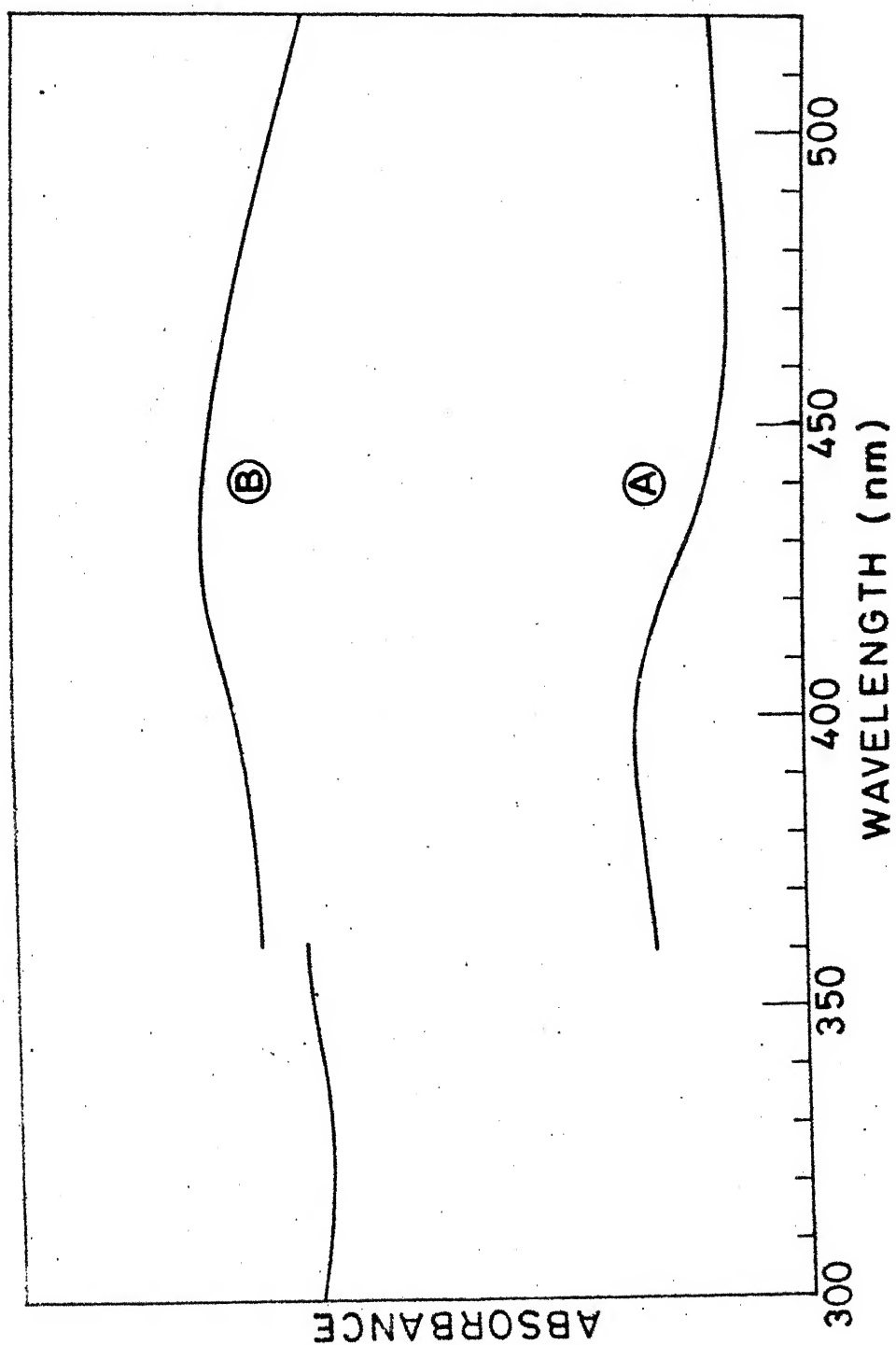


FIG. V.2

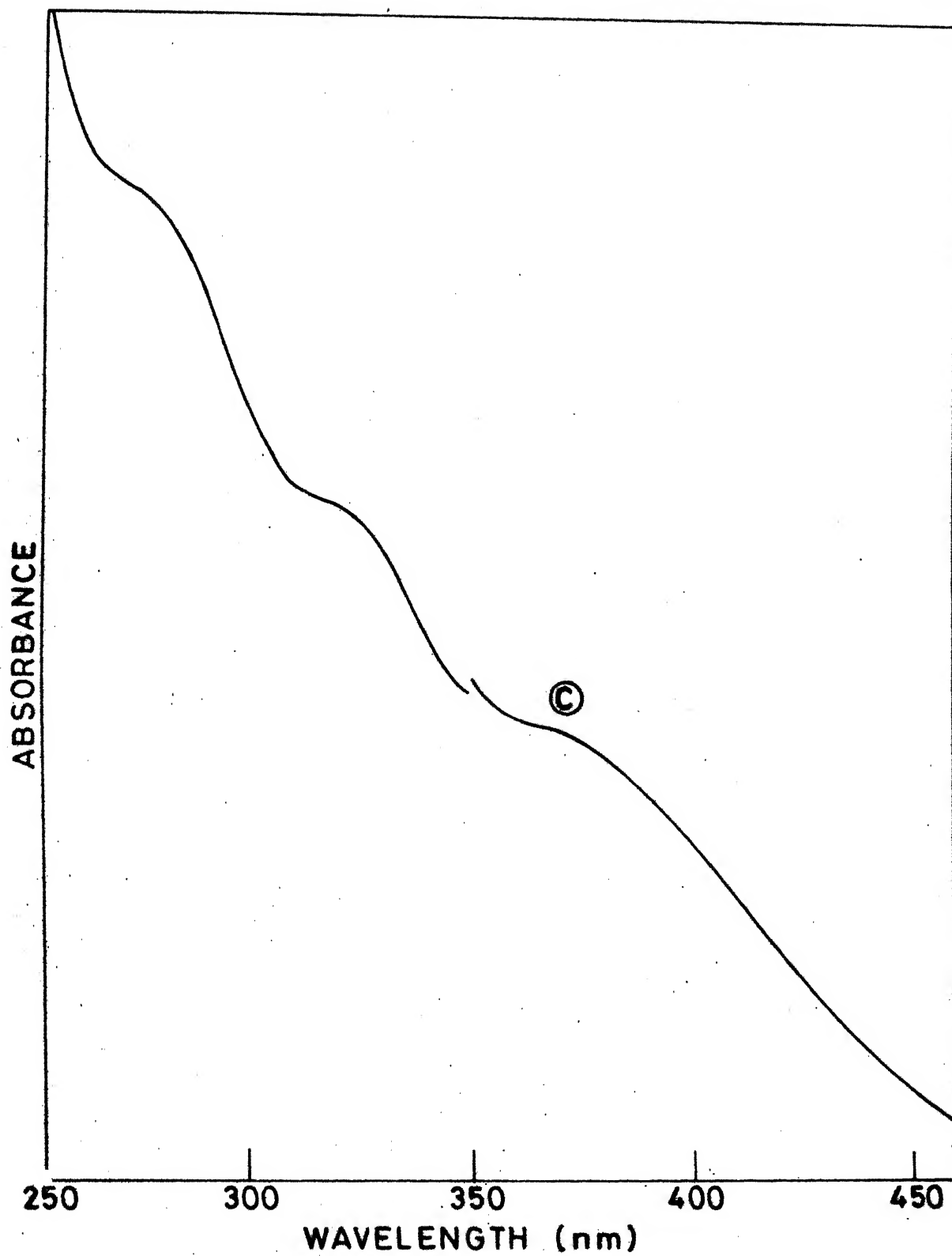


FIG.V.2

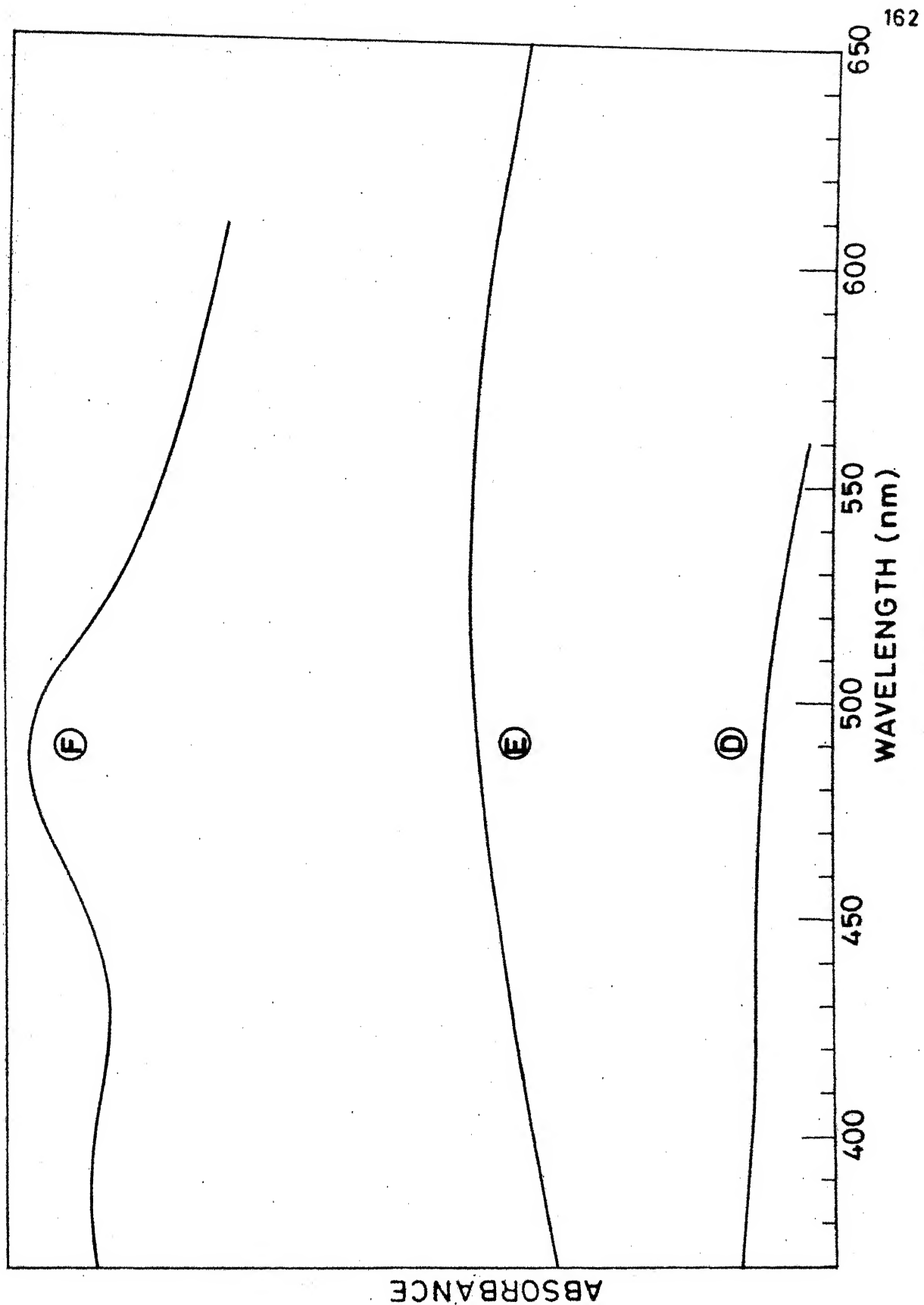


FIG. V.2

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CHAPTER VI

S U M M A R Y

Complexing properties of sulphur containing ligands have been widely studied.¹⁻³ One of the main aims of these studies has been to understand the nature of metal-sulphur bond by correlating the physico-chemical data related to such bond, but there are still a number of gaps which have to be bridged by more experimental data for a rationalisation to be evolved. The work presented in this thesis is only an attempt in this direction. 2-Thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH) have been chosen to study their complexing behaviours towards Cu(I), Cu(II), Ni(II), Co(II), Co(III), Ag(I), Cd(II), Hg(II), Pb(II), Ru(III), Rh(I), Rh(III), Pd(0), Pd(II) and Pt(IV) ions.

First chapter of the thesis presents in brief the salient features of the present situation of the nature of metal-sulphur bond and the chemistry of the complexes formed by the ligands related to the chosen ones.

The complexing properties of TPH and CPTH towards the soft metal ions, $[\text{Cu(I)}, \text{Ag(I)}, \text{Cd(II)}, \text{Hg(II)}, \text{and Pb(II)}]$, have been discussed in Chapter II. Reactions of Cu(I) with TPH in acetonitrile medium yielded a brown coloured complex with the composition, $[\text{Cu(TPH)Cl}]$. It was found to be a diamagnetic solid, stable upto 280°C and to which a linear geometry has been assigned with the ligand bonded through the nitrogen atom of $-\text{C(S)NH-C(O)}-$ moiety.

The reactions of $[\text{Cu(PPh}_3)_3\text{Cl}]$ with TPH initially gave an intense red coloured solution from which the complex $[\text{Cu(PPh}_3)_2(\text{TPH)Cl}]$ has been crystallized out. The physico-chemical data suggested the ligand bonded through nitrogen and a tetrahedral geometry was proposed to this complex. Similar reactions of Cu(I) chloride with CPTH in aqueous ammonia under nitrogen atmosphere yielded a complex, Cu(CPT) in which the ligand acted as deprotonated one as evidenced by the charge-balance and infrared spectrum of the complex. However, the reaction of CPTH with $[\text{Cu(PPh}_3)_3\text{Cl}]$ did not give the expected product as in case of TPH.

Reactions of Ag(I) with both the ligands in water-ethanol solvent at relatively lower temperature gave yellow complexes,

Ag(TP) and Ag(CPT) which were assigned linear (polymeric) geometries. However, on refluxing the complexes in water-ethanol for about half an hour, silver sulphide was precipitated out and from the filtrate, on evaporating followed by extracting the residue in CH_2Cl_2 , the oxidation products of the ligands were obtained which were characterised by mixed melting point, analytical and IR spectral data. The results were further compared with an authentic sample prepared by the literature method. The same observations were also noted when the ligands were allowed to react with other soft metal ions like Cd(II), Hg(II) and Pb(II). In these cases, the pure complexes could not be prepared because of the fast rate of oxidation of the ligands. On refluxing, the pure oxidation products of the ligands were obtained along with the corresponding metal sulphides which were separated and characterised by the procedures similar to those carried out in the reaction of Ag(I) with the ligands. Thus, the observations that the metal ions abstract sulphur from the ligand to yield the corresponding oxygen compounds provide an alternate route for the syntheses of the corresponding carboxi(a)mide. Recently, a mechanism⁵ has been proposed for sulphur abstraction by the metal ions such as Ag^+ , Hg^{2+} , Tl^{3+} in case of S-acetals under similar experimental conditions and the similar mechanism could be fitted for the reactions of sulphur uptake from the thio-carboxa(i)mides by the metal ions.

The third chapter deals with the reactions of cobalt(II) salts with ligands in presence of various nitrogen containing organic bases. Co(II) salts by reacting with the ligand,TPH in H₂O-EtOH medium in the presence of pyridine under refluxing conditions yielded a black-brown coloured complex having composition, [Co(TP)₂Py].2H₂O. Similar complexes were also obtained by using the bases β(γ)-picolines and imidazole. These complexes were found to be stable, slightly soluble in EtOH and acetone, nitrobenzene, DMF or DMSO, insoluble in benzene like solvents and non-melting upto 280°C. However, the reaction of the metal ion with the ligand CPTH in presence of a few drops of pyridine afforded a red diamagnetic complex, [Co(CPT)₂]. Reactions of CPTH with the Co(II) salts in presence of an excess of bases at low temperature (5°C) with stirring gave complexes of the type [Co(CPT)₂B] where B is the organic base. These complexes were found to be bonded through N and O atoms of the -C(S)NH-C(O)- moiety of the ligand where it was acting as bidentate chelating. A square pyramidal geometry has been assigned to these complexes in which the axial position is occupied by the base except for the complex [Co(CPT)₂] which has been given a square planar geometry. The interesting aspect of these complexes has been their diamagnetic behaviour. Co(II) to be diamagnetic in its complexes is unusual and very few such complexes have been known in the literature.⁶⁻⁸ The oxidation state of the cobalt in these complexes has been established as +2, although not

directly, by carrying out the reactions of cobalt(III) complex, $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$ which yielded a paramagnetic complex, $\text{Co}(\text{TP})_2 \cdot 2\text{H}_2\text{O}$, having a magnetic moment value of 1.65 BM which suggested that the ligand under the experimental conditions acted as reducing agent. The value of the magnetic moment of the paramagnetic complex is less than the reported value for the square planar cobalt(II) complex. This could be probably due to the partial dimerisation of the complex through the cobalt-cobalt interaction. The attempts to oxidize the diamagnetic cobalt complexes by bromine in carbon tetrachloride resulted in the decomposition of the complex giving $\text{Co}(\text{II})$ ions and the free ligand. In addition, the same reactions in an inert atmosphere resulted in the formation of a $\text{Co}(\text{II})$ complex of the composition $[\text{Co}(\text{Py})_4\text{Cl}_2]$ and on bubbling dry oxygen or nitrogen gas in the DMF or DMSO solution of complexes, the colour of the solution did not change thus ruling out the possibility of involvement of oxygen in such complexes. The complexes were subjected to infrared as well as electronic spectral studies.

Fourth chapter describes the reactions of $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ salts with TPH and CPTH in presence of pyridine, picolines and imidazole. On refluxing $\text{Ni}(\text{II})$ salts with the ligand TPH in water-ethanol medium for half an hour in presence of organic bases, diamagnetic crystalline stable red products were formed which were isolated and analysed for $[\text{Ni}(\text{TP})_2\text{B}] \cdot x\text{H}_2\text{O}$ which did not melt upto 280°C . They have

been found to be readily soluble in CHCl_3 , CH_2Cl_2 , DMF or DMSO and other similar solvents. On the basis of infrared and electronic spectral studies and in conformity with the literature data, these complexes have been tentatively assigned square pyramidal geometry although trigonal bipyramidal geometry could not be absolutely ruled out. Ni(II) complex of CPTH, Ni(CPT)_2 formed as a result of refluxing of Ni(II) sulphate with CPTH in water-ethanol. It was assigned a square-planar geometry.

Reactions of Cu(II) with TPH in presence of pyridine or imidazole yielded complexes of the type Cu(TP)(TPH)B . These have been assigned a linear polymeric geometry involving N as donor atom. Similar reactions with CPTH have also been carried out. Magnetic measurement studies showed these complexes to be diamagnetic. The diamagnetism and charge balance together with the reducing properties of the ligands suggested that Cu(II) in these reactions got reduced to Cu(I) . Although Cu(II) diamagnetic complexes with antiferromagnetic coupling are known but the former possibility seemed to be more probable.

Fifth chapter includes the reactions of the ligands, TPH and CPTH with the 2nd and 3rd row transition metal ions, viz., Ru(III) , Rh(I) , Rh(III) , Pd(0) , Pd(II) and Pt(IV) . When the hydrated Ru(III) chloride was allowed to react with TPH in water-ethanol under reflux, a complex, Ru(TP)_2 , was isolated. Similar reaction with CPTH in presence of dil. HCl acid gave a

complex, $[\text{Ru}(\text{CPTH})_2\text{Cl}_2]$. Both the complexes were assigned polymeric octahedral geometry. Ru(III) in these reactions was reduced to Ru(II) . Oxidation state of the d^6 Ru(II) complexes has been found to be inconformity with their diamagnetic behaviour. Reactions of $\text{RhCl}(\text{PPh}_3)_3$ with TPH in CH_2Cl_2 yielded a complex, $[\text{RhCl}(\text{PPh}_3)(\text{TPH})]$, which has been assigned a dimeric square planar structure with chloride bridges. TPH is bonded to the metal through carbonyl oxygen in the complex. Rh(III) chloride gave diamagnetic complexes with both the ligands when reacted in an ethanolic solution followed by heating on a water bath. The stoichiometry of these complexes revealed oxidation state of the metal ion to be +1. The formation of Rh(I) from Rh(III) appeared to be in agreement with the reducing properties of the ligands. Palladium and platinum complexes of both the ligands were found to be $(\text{ML}_2)_x$ type which were assigned a polymeric square planar geometry. Infrared spectra of these complexes showed them to be bonded through nitrogen and oxygen of the separate ligand molecules. When the similar reactions were carried out in DMF or DMSO as solvent, metal ion (Pd^{2+}) abstracted sulphur from the ligands and the corresponding oxidation products of the ligand were recovered from the filtrate after separating the metal sulphide. All the complexes have been assigned a tentative geometry based on their analytical results and spectral and magnetic properties. The formulae of the complexes with their geometries, modes of bonding and colours have been given in Table I.1 of the thesis.

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